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Physicochemical Problems in the Preparation of Defect-free Monocrystals of Lanthanum Hexaboride

M.M.Korsukova and V.N.Gurin

The physicochemical basis of the preparation of single crystals of stoichiometric lanthanum hexaboride (a promising new material for emission electronics) is discussed. It is shown that stoichiometric defect-free monocrystals can be prepared only by allowing for the form of the homogeneity region in the phase diagram of the crystalline compound. Studies of defects in the crystal structure are reviewed, and their results are shown to be related to the form of the homogeneity of lanthanum hexaboride. Some physicochemical properties and some possible applications of lanthanum hexaboride monocrystals are examined.

The bibliography includes 150 references.

CONTENTS

I. Introduction

II. Homogeneity region of lanthanum hexaboride and preparation of monocrystals of stoichiometric composition

III. Methods of preparing lanthanum hexaboride monocrystals

IV. Some properties of lanthanum hexaboride monocrystals

I. INTRODUCTION

Lanthanum hexaboride is used in several new instruments (electron microscopes, microanalysers, Auger spectrometers) to study the surface and other properties of materials of various types. However, the preparation of perfect and very pure single crystals of lanthanum hexaboride for use in the cathodes of these instruments still presents some unsolved problems. This is because of the difficulty in controlling the chemical composition and in achieving a high level of structural perfection, and also in establishing adequate quality control.

Many papers have been published on lanthanum hexaboride, dealing mainly with the preparation of LaB_6 monocrystals, with studies of their composition, structure, and properties, and with their emission properties and practical applications. We have recently published a comprehensive review[1] of work on the preparation of LaB_6 monocrystals and on their properties and potential applications, but little emphasis was placed on the physicochemical conditions needed to prepare very perfect LaB_6 monocrystals.

The aim of the present review is to highlight the physicochemical problems underlying the preparation of stoichiometric and defect-free monocrystals of LaB_6.

II. HOMOGENEITY REGION OF LANTHANUM HEXABORIDE AND PREPARATION OF MONOCRYSTALS OF STOICHIOMETRIC COMPOSITION

Though lanthanum hexaboride has been known for a long time,[2] we have little reliable information on the phase diagram of the La–B system and especially on the homogeneity region of LaB_6. The phase diagram of the La–B system was first described by Johnson and Daane,[3] and a modified diagram was subsequently published to include new data.[4] In the most recent publications[5,6] the part of the phase diagram of the La–B system containing the compound LaB_6 is examined. At present two compounds have been reliably identified in the La–B system: 1) LaB_4, which melts incongruently at 2073 K with formation of LaB_6 and of a liquid phase containing 66.7 at.% of B,[3] and 2) LaB_6, which melts congruently at 2988 K.[4,5]

The compound LaB_4 has a tetragonal crystal lattice (UB_4 structure type) with lattice constants $a = 7.324 \pm 0.001$ Å and $c = 4.181 \pm 0.001$ Å;[7] its homogeneity region is very narrow.

The compound LaB_6 has a cubic lattice (CaB_6 structure type).[8] Its crystal structure can be treated as body-centred cubic, with La atoms and octahedra of B atoms occupying positions analogous to those of the Cs^+ and Cl^- ions in the CsCl structure.[9] Each lanthanum atom is surrounded by 24 boron atoms, and each boron atom forms five B–B bonds: four with boron atoms in the same octahedron and the fifth with a boron atom from a neighbouring octahedron.

Published information on the homogeneity region of LaB_6 is inconsistent, and describes the region as broad[3,10] or as relatively narrow.[5,6,11–16] However, in either case the defect structure of the LaB_6 crystal is attributed to defects in the metal (La) sublattice (assumed to be few in the case of a narrow region). The lattice constant of the LaB_6 crystal is found (experimentally) to be unaffected by the defect density.[5,11,17,18] Lastly, some workers have detected a LaB_9 phase with the same structure, and lattice constant, as the LaB_6 phase.[5,19]

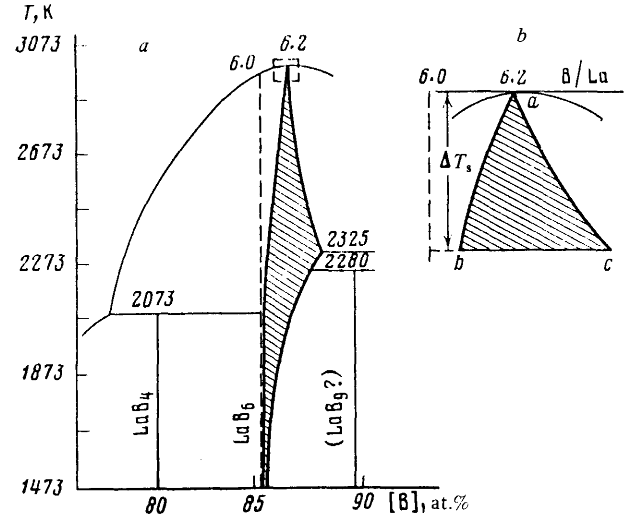

Figure 1. Part of the La–B phase diagram:[5] *a*) is the homogeneity region of LaB_6 *b*) is an enlarged presentation of the high-temperature part of LaB_6 homogeneity region, showing the supercooling ΔT_S.

Existing data on the La–B system suggest a number of conclusions of direct relevance to the preparation of stoichiometric single crystals of LaB_6. Fig.1 shows a part of the phase diagram of the La–B system including the existence region of lanthanum hexaboride.[5] We note that the homogeneity region of LaB_6, which begins at ~2073 K, broadens rapidly as far as 2325 K (the temperature of the LaB_6–B eutectic) and remains fairly wide up to T_m (the melting point of LaB_6) (the "upper" part of the homogeneity region has been described[6] as "narrow" because it is slightly shifted from the stoichiometric composition B/La = 6, and the same description is used in Ref.5). The deviation of the singularity for lanthanum hexaboride from the stoichiometric proportion B/La = 6 is, in fact, substantial: approximately 0.2 atom fraction of B, i.e. to $LaB_{6.2}$. The homogeneity region of the hexaboride is widest (from $LaB_{6.1}$ to $LaB_{6.7}$) at T_{eut} = 2325 K. Inspection of this region near the singularity, i.e. at T_m of lanthanum hexaboride (see Fig. 1*b*), leads to important conclusions regarding the actual composition of the monocrystals obtained from melts at these temperatures (for example, by zone melting).

Thus, if the supercooling of a melt of stoichiometric composition in the crystallisation volume reaches the value ΔT_S the composition of the resulting hexaboride monocrystals is described by the point *b* (for example, $LaB_{6.1}$). Since ΔT_S can vary from a fraction of a degree to hundreds of degrees, and is not easy to control, especially at high temperatures, the composition of the grown crystals can also be uncontrolled. If the composition of the melt at the beginning of the crystallisation corresponds to the point *a* (i.e. to $LaB_{6.2}$) the resulting monocrystals will also have this composition. On the other hand if the initial composition deviates on either side of the point *a* the composition of the resulting crystals will correspond to points on the *ab* or *ac* boundaries of the homogeneity region. This provides our first important conclusion: if the published data[5] for the La–B phase diagram are correct, the preparation of lanthanum hexaboride monocrystals of stoichiometric composition by a liquid-phase method, i.e. from the corresponding melt, is impossible.

Another important aspect of this problem is that the compound LaB_6 dissociates fairly strongly at $T = T_m$. Hence in order to prepare monocrystals from the melt we need to apply an overpressure of a few tens of atmospheres. We also know that at T_m of lanthanum hexaboride the La partial vapour pressure is much higher than the pressure of B.[20] Therefore in order to prepare a melt of the required initial composition (for example, $LaB_{6.2}$) we must introduce the correct B/La component ratio into the initial charge. This means that LaB_6 monocrystals prepared from the stoichiometric melt will always contain an excess of B and consist of a two-phase system or of a solid solution of B in LaB_6. These solid solutions can decompose into LaB_6 and B at low temperatures due to the narrowing of the homogeneity region. This assumption is confirmed to some extent by the presence of B inclusions in LaB_6 monocrystals.[21]

The strong narrowing of the LaB_6 homogeneity region below 2280 K, accompanied by a shift of the left-hand boundary which brings it almost exactly to the stoichiometric LaB_6 composition at 1673–1773 K, suggests another conclusion: LaB_6 monocrystals of stoichiometric composition can be prepared only by methods which are applicable at temperatures not higher than 1673 K.

III. METHODS OF PREPARING LANTHANUM HEXABORIDE CRYSTALS

Only three of the four methods of preparing monocrystals of refractory compounds (according to our classification[22]) have so far been applied to the growth of LaB_6 monocrystals: gas-phase, liquid-phase, and solution methods. We shall consider the special features of each of these methods separately, and compare their technological advantages and their potential suitabilities for the production of stoichiometric monocrystals.

1. The Gas-Phase Method

This method consists in the transport of the substance to be crystallised through the gas phase to the substrate by generating a temperature or concentration gradient between the source and the substrate or by chemical gas-transport reactions. Depending on the chosen method of transport, the monocrystals are grown in a vacuum or in the presence of a carrier. Halogens or halogen–hydrogen mixtures are often used in the preparation of LaB_6 (see Table 1). In any particular method the following crystal growing procedures can be used: a) sublimation, or ΔT transport (when the substance to be crystallised has a high vapour pressure and a congruent evaporation); b) chemical, or Δc transport (when the vapour pressure is low); c) transport of the substance to be crystallised in an electric arc (for a low vapour pressure and a high melting point); d) chemical reaction in the gas phase (in which the synthesis precedes the crystallisation of the substance). Only Δc transport[23,24] and chemical reactions[25,26] have been used so far, from the above list, to prepare LaB_6 monocrystals:

$$La_2O_3 + H_2 + BCl_3 \rightarrow LaB_6 + HCl$$

$$LaCl_3(g) + 6BCl_3(g) + (21/2)H_2(g) \rightarrow LaB_6(s) + 21HCl$$

Table 1. Preparation of LaB_6 monocrystals by the gas-phase method.

Method of preparation	Preparative conditions			Characteristics of the resulting crystals		Refs.
	T, K	time, h	other conditions	shape and size, mm	other characteristics	
Δc transport Br_2 carrier	1423–1173	–	initial charge LaB_6 powder, Ar inert gas	needles; 0.50 × 0.15 × 2.00	colour violet	[23]
Δc transport carriers (H_2 + BBr_3) or H_2 + Br_2)	1273–1573	–	initial charge LaB_6, substrate sintered LaB_6	⟨100⟩ whiskers, pyramidal crystals	–	[24]
Chemical reactions	zone *A* 1273; zone *B* 1623–1723	3	initial charge pressed La_2O_3; substrate graphite	{100}cubes, {111}cubo-octahedra; 1 × 1 × 1	colour purple	[25]
Chemical reactions	1373–1623	0.5–2	substrate graphite, $BCl_3/LaCl_3$ = 10:1, atmospheric pressure	⟨100⟩ whiskers; l = 2–5, thickness 0.001–0.020; ⟨100⟩ pyramids	colour purple (lattice constant a = 4.151 A); colour blue (lattice constant a = 4.155 A)	[26]

The control of crystal growth processes is complicated by the need to monitor and control several factors within closely specified limits: the rates of evaporation, the concentrations of the initial components in the carrier gas, the temperature gradient, etc. Data on the preparation of LaB_6 monocrystals by the gas-phase method are shown in Table 1.

The possibility of growing oriented and regular whisker structures of various elements and compounds by a gas-phase method, using Δc transport, is of great practical interest.[24]

The results in Table 1 show that LaB_6 monocrystals produced by the gas-phase method are usually facetted, and grow preferentially in a <100> direction. However, they tend to be small, and difficult to use as single-crystal samples in physical experiments. Furthermore, their precise chemical composition has never been reported, except for a list of impurities.[26] The same paper[26] gives the lattice constants of the LaB_6. Most other reports merely describe the colour of the crystals, which varies from purple to blue, the latter being ascribed to an excess of boron in the sample. However, this interpretation cannot be tested unambiguously because of the lack of chemical analyses. In view of the relatively low temperatures and other conditions used in the gas-phase method, and noting the data on the homogeneity region in Fig.1, it would appear that stoichiometric LaB_6 crystals can be produced, in principle, by this method. The main difficulty here is the need for exact control over the initial concentrations, which determine the La : B ratio in the monocrystal, and also the need for fine adjustment of many other factors (mentioned above) known to affect the stoichiometry of the growing LaB_6 crystals.

Another shortcoming of the gas-phase method (especially for the growth of crystals by using chemical reactions) is the possibility of co-depositing impurity phases such as boron with the LaB_6. As reported,[26] this danger can be avoided by using a BCl_3 concentration much lower than the value corresponding to the stoichiometric ratio $BCl_3/LaCl_3$ = 6. The coprecipitation of boron is entirely suppressed at $BCl_3/LaCl_3 < 2$.

The gas-phase method has not so far produced monocrystals of adequate quality and size. However, further developments (including the use of seed crystals) may result in the production of large and perfect LaB_6 crystals. Another promising line of research is aimed at the production of regular whisker structures of LaB_6, which may find practical application.[24]

2. The Liquid-phase Method

The liquid-phase method consists in passing the substance to be crystallised through a heated zone in which a temperature gradient is maintained, or in moving the zone relative to the sample. The compound, which can enter the zone either in the liquid or in the solid state, is first melted and then crystallised. The wide variety of possible technological variants of this method has led to the development of a large number of different techniques for growing single crystals.[22]

Only the zone melting method has been used for growing monocrystals of LaB_6, in the crucible-free form which avoids contact between the hexaboride melt and any container material. Data on the preparative conditions and characteristics of LaB_6 monocrystals prepared by zone melting are summarised in Table 2. The ingot for zone melting is previously prepared as a rod of the required diameter: the quality of the final product is largely determined by the composition and purity of these ingots. Various heating methods are used to generate the molten zone in the sample. Thus, relatively large (4–7 mm in diameter) monocrystals (or polycrystalline ingots) have been obtained with high-frequency[27,31] or electron-beam heating.[21] Thinner monocrystals (~1 mm diameter or less) have been prepared successfully by electric arc or laser methods of heating.[28] Dissociation and evaporation of the LaB_6 are avoided by carrying out the zone melting operation in an atmosphere of purified gas (usually argon).[27–30] Nitrogen, hydrogen, and helium have also been used.[21] The concentration of impurities can be lowered to the 10^{-3}–10^{-4}

wt.% level by repeated zone passes (see Table 2). It is reported[29] that a single zone pass can lower the impurity concentration (transition metals of Groups IV–VIII, Cu, Al, Ca, etc.) by a factor of 13–69, i.e. almost to the 10^{-2}–10^{-3} wt.% level, increasing to a factor of 315 (10^{-3} wt.%) after three passes.

Table 2. Preparation of LaB_6 monocrystals by the liquid phase (zone melting) method.

Preparative conditions			Characteristics of the monocrystals		Refs.
composition of initial billet c^{p}_{Σ}, wt.%	atmosphere; pressure, mmHg	formula	impurities, wt.%	growth direction; crystal size, mm	
LaB_6: 99.9	Ar; $1.1 \cdot 10^4$	LaB_6	non detected (3 zone passes)	not determined; $l = 60$, $d = 7$	[27]
$LaB_6 > 99.0$; $LaB_6 + (1.6-2)$	N_2; 20	La_xB_6, where $0.85 < x < 1.0$	$c^{p}_{\Sigma} < 0.1$ (microprobe) (1 zone pass)	not determined; $l = 25$, $d = 3.6$	[21]
LaB_6; $c^{p}_{\Sigma} = 0.485$	Ar; 760	–	$c^{p}_{\Sigma} = 0.043$ (2 zone passes)	⟨100⟩; $l = 60$, $d = 1.1$	[28]
$LaB_{6.00\pm0.03}$; $LaB_{5.99}$ and $LaB_{5.81}$	Ar; 52	$LaB_{6.00\pm0.15}$, $LaB_{5.86}$, $LaB_{5.72}$	$c^{p}_{\Sigma} = 0.0045$ (3 zone passes)	⟨100⟩; $l = 23-26$, $d = 0.25-1.50$	[29, 30]
$c^{p}_{\Sigma} = 1.125$	inert gas	LaB_6	$c^{p}_{\Sigma} = 0.015$	not determined; $l = 120$, $d = 7$	[31]
La + B; $c^{p}_{\Sigma} = 1.6$	Ar; 760	$LaB_{5.9}$, LaB_6	$c^{p}_{\Sigma} = 0.01$ (3 zone passes)	deviation from ⟨111⟩ 5°; $l = 120$, $d = 10$	[32, 33]

Notes: c^{p}_{Σ} is the total impurity concentration; l is the length and d is the diameter of the crystal.

In most of this work the initial LaB_6 had a stoichiometric composition. However, some workers used specially prepared initial samples which were deficient in lanthanum (i.e. contained added boron). In this way it was shown[21] that in order to produce good-quality billets boron powder must be added to the LaB_6 powder (2 mole boron to 1 mole LaB_6). The resulting monocrystals were of good quality, but they contained an excess of boron as well as the LaB_4 phase. The presence of LaB_4 can be attributed to the high rate of crystallisation used in those experiments,[21] which was an order of magnitude greater than normal values.

The LaB_4 had an oriented distribution, and its presence had almost no effect on the sharpness of the Laue diagrams of the LaB_6 monocrystals. A seed crystal containing an excess of boron (86.9% B) was used[28] in addition to seeds of stoichiometric composition. By studying the melting points of the samples it was concluded that the composition of the crystals corresponding to the highest melting point is shifted from the stoichiometric value towards the boron-rich side. This observation anticipated the publication[5] of the phase diagram of the La–B system. In addition, the LaB_4 phase was detected in samples prepared from billets of stoichiometric composition. Its presence was attributed to incongruent melting of the LaB_6.

As was stated above, according to data[5] obtained by the liquid-phase method (see Fig.1), the preparation of stoichiometric LaB_6 by this method (including zone melting) is impossible even when non-stoichiometric initial ratios of La to B are used to allow for differences in evaporation rate at the growth temperature. However, some workers[27,31,33] have assigned the formula LaB_6 to their lanthanum hexaboride crystals on the basis of chemical analysis (and within the precision of that method, see Table 2). We should stress that, unfortunately, the exact quantities of B and La in the resulting LaB_6 monocrystals are not stated in those papers, and no indication is given of the precision of the chemical analysis. Therefore it is difficult to establish the exact ratio of B to La in those samples and the exact formula of the hexaboride.

This shortcoming is not found in an analytical investigation[30] specially aimed at determining the stoichiometry of the grown LaB_6 crystals (see Table 2) and at identifying the impurities in the samples. All the monocrystals were found to be deficient in boron both in respect of their stoichiometric composition and in respect of the composition of the initial ingot, but they were free from inclusions of the LaB_4 phase. Relatively large amounts of carbon were detected in the crystals. The low boron content was attributed[30] to the formation of a compound between boron and carbon by the reaction of carbon with the LaB_6 melt (but no experimental evidence for this suggestion is given). On the evidence of chemical analysis and density data these workers concluded that the boron sublattice contained defects and that La atoms could be accommodated in the sites of the missing octahedra of boron atoms.

Thus the liquid-phase method can be used to prepare reasonably large monocrystals of high purity, but it has serious disadvantages such as a variable and non-stoichiometric composition of the resulting LaB^6 crystals and the presence (in some cases) of LaB_4 and B inclusions.

3. Crystallisation from Solutions

The solution method consists in the mass (or seeded) crystallisation of refractory compounds from metallic, salt, or hydrothermal solutions. The crystallisation takes place at a fixed (or variable) solution supersaturation, produced by evaporating the solvent or by lowering the temperature and by the corresponding decrease in solubility of the substance to be crystallised. The crystallisation is controlled by using a seed crystal immersed in the solution, and by establishing special regimes of solvent evaporation and cooling the system or adding feed material to it.[22]

The variants of this method differ in the nature of the solvent (elements, compounds, metals, salts) and in its relationship to the solute (i.e. in its ability to form compounds with it).[22] One of the main attractions of the solution method is the possibility of obtaining different morphological modifications of the monocrystals (needles, plates, isometric crystals), and also the relatively low temperatures of the growth processes and their technological simplicity. So far, only crystallisation from solutions in metallic melt and electrocrystallisation have been used to prepare monocrystals by the solution method. Information on the crystals prepared by these methods is given in Table 3.

Let us examine in greater detail the solution method, which appears to offer the most promising possibilities for the production of stoichiometric LaB_6 crystals. To control the crystallisation of LaB_6 from solution in Al we need information on the phase equilibria in the ternary La–B–Al system at different temperatures, and also data on the polythermal section of the LaB_6–Al phase diagram. If these data are available we can establish the following:

1) the temperature dependence of the solubility of LaB_6 in an Al melt;

2) the phase relationships and interconversion during crystallisation.

However, the phase diagram of the La–B–Al system has not so far been determined. The reported[46] isothermal section of the phase diagram at 873 K shows that ternary compounds are not formed on this section and that the LaB_6 is in equilibrium with the Al, indicating the possibility of preparing LaB_6 crystals from the Al melt. Since the LaB_4–Al equilibrium does not appear on the isothermal section, the LaB_4 phase cannot crystallise and contaminate the LaB_6 crystals. There is no information on the temperature dependence of the solubility of LaB_6 in an aluminium melt: the composition of the initial charge is usually calculated approximately by equating the solubility of LaB_6 to that of boron in aluminium at the given temperature. This estimate is only a rough approximation, and apparently too high, but at present we have no better way of defining the crystallisation regime of the LaB_6.

An overall representation of the crystallisation regimes can be based on the data in Fig.2, which shows a polythermal section with a metastable region in the phase diagram of refractory compound (MN)–solvent metal (R) systems, together with possible variants of the mass crystallisation regime.

The metastable region, defined by the full curves, is divided into two parts by the dot-and-dash curves, corresponding to the spontaneous formation of singlet nuclei (part *I*, temperature range T_1–T_2) and to massive nucleation (part *II*, range T_2–T_3), but not so massive as in the labile region below T_3. After being heated to the required temperature and held at that temperature for the time needed for the synthesis and homogenisation of the molten solution the system can be cooled according to several regimes, of which the most effective is $A_1B_1C_1D_1$. After a hold at the temperature A_1 the system is rapidly cooled to the temperature B_1 to form a relatively small number of nuclei, then the temperature is raised to C_1 to redissolve the more unstable nuclei (in order to decrease the number of nuclei and thus obtain larger crystals), and lastly the system is cooled along the line C_1D_1, which is parallel to the solubility curve of the crystallising compound. Other regimes (see Fig.2) yield smaller and less perfect monocrystals, and are only used for special reasons.[47]

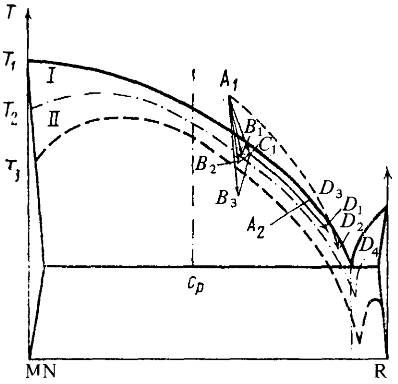

Figure 2. Metastable region (diagrammatic) in a polythermal section of the MN–R phase diagram and mass crystallisation regimes (from Ref.47).

LaB_6 monocrystals of stoichiometric (or near-stoichiometric) composition are obtained by crystallising the system by the solution method according to the LaB_6–Al polythermal section (Fig.3), starting from the temperature 2073 K at which the left-hand edge of the homogeneity region begins to follow the stoichiometric composition towards lower temperatures. This

Table 3. Preparation of LaB_6 monocrystals by the solution method.

Initial components			Preparative conditions			Characteristics of monocrystals			Refs.
Composition (wt.%); weight of solvent (g)	purity of B and La (wt.%); B/La ratio	c, wt.%	T, K	t, h	ν K h^{-1}	shape and size of crystals, mm	method of analysis; formula	cp c^{p}_{Σ}, wt.%	
Al (99.9999) —	B (99.99), La (99.9); 6:1	13.35	1773	0.16	25	needles 5.0–7.0 × 0.1 × 0.1; plates 2.00 × 3.00 × 0.05; cubes	—	0.01	[34.35.36.37]
Al(99.9); 90—140	B (99.99), La (99.9); 4.98:1	2.4÷3.6	1473	5÷10	6.2÷75	needles 5.0 × 0.5 × 0.5; plates; cubes	—	0.045	[38]
Al(99.8); 58	B (99.8), La 99.5) 5.8:1	3.06	1773	8	30	needles; plates; cubes	—	0.005—0.01	[39]
Al(99.99); —	B (>99), La (>99); 6:1 or 12:1	5÷10	1573—1673	2÷10	—	needles 10.0 × 0.5 × 0.4; plates 6.00 × 7.00 × 0.15; cubes 1.90 × 0.85 × 0.85	chemical analysis**; $LaB_{5.86}$ (31.0 wt.% B); $LaB_{6.04}$ (32.0 wt.% B)	0.056 (Al)	[40—43]
Al; 41	B (99.9), La_2O_3; (4÷8):1	10	1773	120	5÷20	needles 5 × 1 × 1; plates 2.0 × 2.0 × 0.1; cubes 1 × 1 × 1	microprobe; (30.00 ± 0.08 wt.% B)	—	[44]
*—	—	—	1073	200÷300	no cooling	cubes 6 × 6 × 5	microprobe; $La_{0.67}B_6$÷$La_{0.87}B_6$	—	[45]

Symbols: *c* is the concentration of LaB_6 in solution, *t* is the hold time, ν is the cooling rate.

*Crystals prepared by electrocrystallisation from molten salts (melt composition, mole %: La_2O_3 0.1–4, B_2O_3 33.5, Li_2O 31.2, LiF 33.1.

**The calculated boron content of LaB_6 is 31.8 wt.%.

property of the system imparts some substantial advantages to the solution method as compared with other methods of producing LaB_6 crystals of stoichiometric composition.

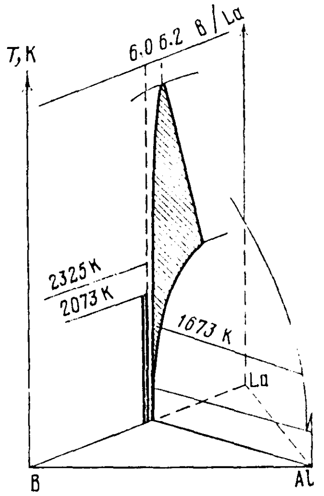

Figure 3. Polythermal section (diagrammatic) of the LaB_6–Al phase diagram (from Ref.47).

The LaB_6 crystals are usually prepared as follows. Known weights of boron and lanthanum (in stoichiometric proportions) are placed in an alundum crucible or boat together with the aluminium, heated in an argon atmosphere to the required temperature, held at this temperature for several hours in order to homogenise the melt, and after rapidly lowering and again raising the temperature the system is brought to 873 K by forced cooling (see Fig.2).[47] The fundamental condition for successful crystallisation is that the point $B_{1(2)}$ must always lie within the metastability region (preferably, in its upper part). The following mass crystallisation regimes can be defined (Fig.2): $A_1B_1C_1D_1$ (the optimum); $A_1B_2C_1D_1$ (a possible regime for a broad homogeneity region of the crystallising substance); A_1D_2 (an "incorrect" regime, leading to the deposition of very small crystals); $A_2D_3D_4$ (a possible regime for a low synthesis temperature).

After being cooled the aluminium ingots are dissolved in dilute HCl, NaOH, or KOH to isolate the LaB_6 crystals. La_2O_3 can be used as one of the initial components instead of metallic La: in this case the reaction $La_2O_3 + B + Al \rightarrow LaB_6 + Al_2O_3 +$ other products takes place in the aluminium melt.[44,48]

In the temperature range 1473–1773 K (see Table 3) the LaB_6 crystallises from solution in an Al melt in three morphological modifications: needles, plates, or isometric cubic crystals (Fig.4*a* and 4*b*), the needles and plates being much larger than the cubic crystals. It was reported[38] that under stated experimental conditions (see Table 3) the needle-like crystals greatly outnumber those of other morphologies. For example, at a cooling rate of 75 K h^{-1} the numerical ratio of the crystals of different habit (needles : plates : cubes) was 76 : 23 : 1. It is also reported[43] that this ratio depends on the concentration of LaB_6 in the Al: increasing the concentration increases the proportion of platelets in the crystals.

From the Laue patterns of the crystals it was concluded[49] that the plates and needles have {100} cube faces, i.e. the plates have a large (100) face (several mm^2 in area) and the needles are elongated in the <100> direction. This is confirmed by data on the etching behaviour of the monocrystals.[38,42] Some crystals have smooth faces, others show conical projections and growths steps, and skeletal growth forms are also found (in the shape of hollow cubes and needles), denoting a high degree of supersaturation during the growth (Fig.4*b*). It was shown[49] that many monocrystals have a block structure, with a maximum mis-orientation of 2° in platelets and much smaller (~10′) in needles (the mis-orientation of the blocks was calculated from photographic enlargements of the Laue spots).

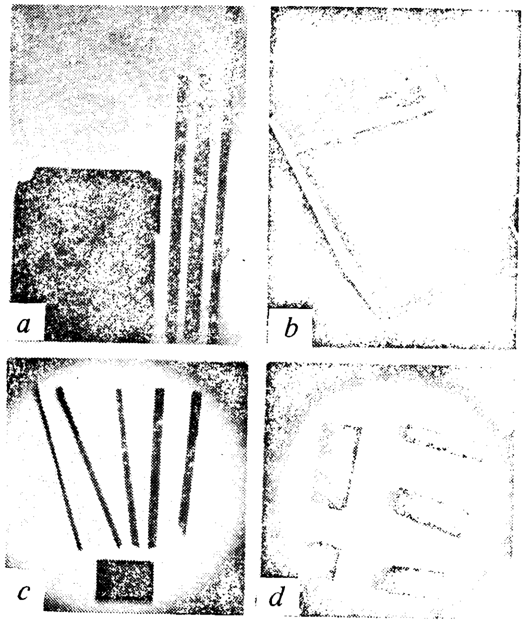

Figure 4. General shape of monocrystals of lanthanum hexaboride and of solid solutions of the $La_{1-x}M_xB_6$ type crystallised from aluminium: *a*) needles and plates of LaB_6; *b*) cubic LaB_6 crystals; *c*) $La_{1-x}Ce_xB_6$ solid solution; *d*) $La_{1-x}Tb_xB_6$ solid solution; magnification x6 (*a*, *c*, *d*) and x500 (*b*).

The composition of the LaB_6 monocrystals was determined quantitatively only in two investigations,[42,44] aiming to establish the effect of the B/La ratio in the initial ingot on the composition of the resulting crystals. In one of these studies[42] chemical analysis showed that the composition of the crystals obtained for a stoichiometric initial ratio of the components generally corresponds to the formula $LaB_{6.0}$. An initial ratio of 12 : 1 yields crystals deficient in boron ($LaB_{5.86}$). Other workers[44] varied the B/La ratio between 4 : 1 and 8 : 1 but could not detect any difference between the compositions of the resulting crystals. The reported composition in this case corresponded to a deficit of boron in the lanthanum hexaboride crystals. We should stress that in spite of the use of an excess of boron in the initial charge there has not been a single report of the deposition of a LaB_9 phase by crystallisation from an Al melt.

Aluminium inclusions have been detected in some LaB_6 crystals.[38,42] This type of solvent entrainment is observed at high rates of growth of the crystals from solution.[50] The crystallisation regime should be defined so as to avoid the formation of extraneous inclusions.

The crystallisation from Al solutions yields lanthanum hexaboride crystals of various colours: from a bright purple to violet and blue. There have been attempts to associate the blue colour with the presence of finely divided inclusions of free boron[13] or with a small lanthanum defect[3,6,19] (for example, the La content was found[6] to be 66 wt.%). However an X-ray microprobe analysis of crystals of different colour prepared by the solution method detected identical boron concentrations in all the crystals.[44] It was reported[49] that after brief etching in dilute HNO_3 all the crystals display a bright purple colour gradually turning to blue on long exposure to air. The conclusion[44,49] was that the differences in colour between the crystals are due to differences in the state of the surface (mainly, the presence of an oxide film).

The total impurity content of these LaB_6 monocrystals according to spectrographic analysis is 0.005–0.05 wt.% (see Table 3), i.e. fully comparable with the purity of the crystals prepared by zone melting (Table 2). Obviously, even purer crystals can be prepared from purer starting materials by exploiting the distribution coefficients of the various impurities.

LaB_6 monocrystals containing the ^{10}B and ^{11}B isotopes, needed in various investigations,[49] have also been prepared by crystallisation from a solution in molten Al.

In an attempt to improve the emission properties of LaB_6 cathodes, monocrystals of solid solutions of the type $La_{1-x}.M_xB_6$ have been prepared,[40,44,48,51,52] where M is a rare-earth (Ce, Gd, Tb, Pr, Nd, Sm, Dy, Y) or an alkaline earth metal (Ba), and x varies between 0.02 and 0.70 atom fraction. These are similar in size to the pure LaB_6 crystals (needles and platelets, see Figs.4c and 4d). It was reported[44] that the composition of the solid solution crystals is not exactly correlated with the initial component ratio. The discrepancy between the initial LaB_6/MB_6 ratio and the composition of the crystals can be as high as ±15 mole % in some crystals. Other workers[52] find this scatter to be less than 8 at.%.

Another method (electrocrystallisation from molten salt solutions) has been used to prepare fairly large cubic monocrystals of LaB_6 (see Table 3). The most significant feature of this method is that electrolysis of the molten salts (or oxides) is carried out at constant temperature. The driving force of the crystallisation process is the applied potential gradient. Electrolysis has been carried out at a constant voltage between 1.85 and 2.1 V, which gives the cathodic current density (20–40 mA cm^{-2}) needed for crystal growth. Unfortunately, the composition and impurity content of the LaB_6 crystals (grown on a seed) is not quoted,[45] and these results cannot be compared with those obtained by other methods.

A comparison of all the methods of preparing lanthanum hexaboride crystals (Table 4) shows that the highest temperatures are used in the liquid-phase methods; in the gas-phase and the solution methods the maximum temperatures are similar, and lower than T_m for lanthanum hexaboride by almost a factor of two; the liquid-phase method offers the highest rate of growth of monocrystals. Though each of these methods (in principle) can be used, with appropriate seeds, to grow single crystals oriented in any required crystallographic direction, this has been achieved, in practice, only in the liquid-phase method. Different morphological modifications of idiomorphic monocrystals can be obtained only by the solution method. The limiting impurity concentrations in monocrystals prepared by the different methods are approximately equal. Allowing for the shape of the LaB_6 homogeneity region (especially in crystallisation by the solution method) leads to the production of stoichiometric or very nearly stoichiometric monocrystals. The liquid-phase method often produces inclusions of LaB_4 and B, while inclusions of Al are obtained when the solution method is used.

The most perfect monocrystals are grown by the solution method, with the smallest block misalignment and the lowest dislocation density. Single crystals of a prescribed shape can be prepared only by solution and by liquid-phase methods (in the latter case, by using Stepanov's profiling method[53]). These aspects should not be forgotten when comparing the future prospects of the various methods. On the whole it is difficult to identify any one method as superior to all others. Each method has its advantages and disadvantages, and each can yield monocrystals of adequate quality. In view of the practical requirement for monocrystals in needle or platelet form for the preparation of hot or cold emission cathodes, and of the difficulty of growing those crystals by the liquid-phase method, the solution method of growing LaB_6 crystals of stoichiometric composition offers some advantage over the other methods.

Table 4. Comparison of methods of preparing LaB_6 monocrystals.

Parameters	Methods		
	gas phase	liquid phase	solution
	Preparative conditions		
Temperature range, K	1273–1723	above 2988 (degree of superheating not quoted)	1073–1773
Growth time or rate of pulling (or cooling)	0.5–3 h	18–420 mm h^{-1}	5–75 K h^{-1}
Other features and prospects of the method	preparation of oriented regular structures	growth on seeds	growth of crystals in a prescribed orientation; electrocrystallisation
	Characteristics of resulting monocrystals		
Maximum size, mm	$l = 5$ (needles), $d = 2 \times 10^{-5}$	$l < 120$ (rods), $d = 1–10$	needles 10.0 × 0.5 × 0.4; platelets 6.00 × 7.00 × 0.15; cubic crystal 6 × 6 × 5
Impurity content, wt.%	at the limit of sensitivity of the microprobe	$10^{-1}–10^{-4}$	Al up to 2×10^{-1} – $(5–10) \times 10^{-3}$
Structural perfection (misorientation of the blocks)	no data	between 20″ and a few degrees	platelets up to 2°, needles up to 10′
Dislocation density, cm^{-2}, and face	$10^4–10^5$; (100)	$10^6–10^7$; (100)	$10^3–10^5$; (100)
Possibility of preparing monocrystals of stoichiometric composition	yes	no	yes

These conclusions are confirmed by X-ray structural studies[17,54,55] of three LaB_6 monocrystals prepared by the solution method with different B/La ratios in an Al melt and at different temperatures (B/La = 9:1 and 5:1 at 1673 K; B/La = 9:1 at 2073 K). The results on the crystal structure of LaB_6, shown in Table 5, were unexpected. Instead of defects in the lanthanum sublattice, which could have been expected in boron-rich compositions,[3,10] full occupancy of the lanthanum positions and a small defect density in the boron sublattice were observed in all three crystals, irrespective of their composition. It follows that the data on the homogeneity region of LaB_6 (see Fig.3), at least those at 2073 K and below, need to be re-examined: it appears that the boundary coinciding with the line of stoichiometric composition should be the right (rather than the left) solidus line. With this exception the shape of the homogeneity region should be as outlined in Ref.6.

Table 5. Data on the structure of LaB_6 (from Refs.54 and 55).

Structure parameters	Crystal No.1	Crystal No.2	Crystal No.3
Position of boron atom, x_B	0.19956 (16)	0.19957 (15)	0.19948 (14)
Occupancy and position factor of the boron, %	96.4 (7)	97.2 (5)	98.2 (5)
Isotropic temperature factor of the lanthanum U_{iso}, Å^2	0.00535 (3)	0.00551 (2)	0.00525 (2)
Anisotropic temperature factor of the boron, Å^2: U_{11} $U_{22} = U_{33}$	0.0031 (2) 0.0044 (2)	0.0032 (2) 0.0046 (1)	0.0031 (2) 0.0046 (1)
Divergence factor R, %	1.36 (935 reflections)	1.10 (1224 reflections	1.15 (1190 reflections)
B/La atomic ratios:			
from X-ray analysis data	5.76	5.80	5.86
from chemical analysis data	5.7	—	6.8

Notes. The standard errors are shown in brackets. The following initial ratios in the melt and temperatures were used: crystal No.1, B/La = 9:1, T = 1673 K; crystal No.2, B/La = 5:1, T = 1673 K; crystal No.3, B/La = 9:1, T = 2073 K.

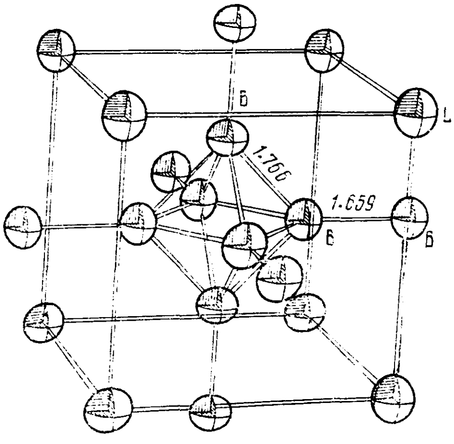

Figure 5. Crystal structure of LaB_6; the thermal vibration ellipsoids of the atoms are taken from Refs.54 and 55.

Another important result of these studies[54,55] is the recognition of a large anisotropy in the thermal vibrations of the boron atoms (see Fig.5 and Table 5). It is clear that the thermal vibrations of the boron atoms are weaker in the direction of the bond between octahedra than in the direction of the bonds within the octahedron. This conclusion is consistent with the results of studies of LaB_6 monocrystals by Raman spectroscopy,[56,57] according to which the force constants of the B–B bonds between octahedra and within the octahedra are 2.18 and 1.28 mdyn Å^{-1} respectively. We should also stress that the amplitude of the thermal vibrations of the La atoms is greater than that of the B atoms (see Table 5). This suggests a rigid boron sublattice with lanthanum atoms vibrating relatively freely in its interstitial sites. These aspects of the crystal structure of lanthanum hexaboride are responsible for many of its properties, discussed in the next section.

IV. SOME PROPERTIES OF LANTHANUM HEXABORIDE MONOCRYSTALS

In this section we shall aim as far as possible to discover the relationship between the properties and the composition of LaB_6 monocrystals.

1. Electrophysical Properties

The electrophysical properties of LaB_6 monocrystals have been studied mainly on samples prepared by zone melting.[27,58,59] The results confirm the metallic nature of LaB_6, previously established for polycrystalline samples.[10] Hall effect measurements on samples of two types (prepared with 1 pass and 3 passes of the molten zone respectively) gave the same value of the Hall constant (R_H) in both cases: in other words, this constant is independent of the purity of the crystals.[27] The carrier concentration calculated from R_H is ~1 electron per La atom, which agrees with the band structure of the hexaborides of tervalent rare-earth metals suggested in the early publications.[60,61] An important characteristic of LaB_6 monocrystals is the ratio of the electrical conductivities at 300 and 4.2 K ($\rho_{300}/\rho_{4.2}$). We know that the electrical conductivity of metals at room temperature is determined mainly by the scattering of the conduction electrons on acoustic phonons, whereas at liquid-helium temperatures it is determined by scattering at impurity atoms and lattice defects.[62] Therefore this ratio is very sensitive to the quality of the crystals: the fewer impurities and defects are present in the crystal, the lower will be the residual electrical resistance $\rho_{4.2}$, and the higher the ratio $\rho_{300}/\rho_{4.2}$. Thus, for melted polycrystalline samples (1 zone pass) containing 10^{-1}–10^{-2} wt.% of impurities the ratio was 20–45,[27,59] whereas for the purer monocrystals (3 zone passes) containing ~10^{-3}–10^{-4} wt.% of impurities the ratio was 200–450,[27,58] and even as high as 740.[63] In monocrystals prepared by the solution method the ratio $\rho_{300}/\rho_{4.2} \cong 200$ [35] corresponds to the lower limit for the zone-melted crystals. However, we should remember that the error in measuring this quantity may be large in the case of small crystals.

A study[58] of the temperature dependence of the electrical resistance of a zone-melted monocrystal ($\rho_{300}/\rho_{4.2} = 450$) in the range 360–4.2 K has shown the need to allow for the contribution from the scattering of electrons on optical phonons, which becomes appreciable at ~100 K. At 300 K this contribution accounts for ~30% of the total resistivity of the LaB_6. The scattering of electrons on optical phonons is an important difference between LaB_6 and metallic elements, which confirms the ionic nature of the interactions between the boron and lanthanum sublattices.[60] A study of the dynamic resistance of a LaB_6 monocrystal at 1.7 K by the point contact spectroscopy method confirmed the predominance of electron–phonon interaction processes in the scattering of electrons.[64]

Experimental studies of magnetoresistance and of the de Haas–van Alphen effect have been made on monocrystals prepared by solution and liquid-phase methods,[35,63,65] using models of the Fermi surface for LaB_6 which were consistent both internally and with calculations of the band structure of LaB_6.[66,68] According to those measurements[35,63,65] the conduction band of LaB_6 is very wide, and the conduction electrons have a negligibly small *s* character owing to the hybridisation of the 5*d* orbitals of the lanthanum atoms with the 2*s*–2*p* orbitals of the boron atoms. A study of the energy structure of the valence band by determining the angular dependence of the photo-emission from the (100) faces of a LaB_6 single crystal prepared by zone melting[69] revealed the presence of several sub-bands in positions agreeing to within ~0.5 eV with calculated results.[67]

Information on the band structure can also be obtained from the reflectance spectra, which have been studied on polycrystalline samples prepared by zone melting and on films of LaB_6 in the energy range 0.05–6 eV.[25,70–74]

2. Optical Properties

The optical properties of LaB_6 monocrystals were first studied over a wide range of energies (0.05–40 eV) on laminated crystals (mosaics of platelets) prepared by the solution method.[75,76] The reflectance spectrum of LaB_6 (curve *1* of Fig. 6*a*) shows a deep minimum at an energy of 2.1 eV, due to the interaction of light with the conduction electrons. It corresponds to a sharp maximum in the loss function ($-\mathrm{Im}\,\varepsilon^{-1}$, curve *3* of Fig. 6*b*). At energies greater than 2.1 eV we observe a steep increase in the imaginary part of the dielectric constant ε_2 (curve *2* of Fig. 6*b*), indicating band-to-band transitions (direct band gap) of the electrons from the valence band to the conduction band, whose lowest levels are filled with electrons. Hence the spectra of the optical constants in present energy range are determined both by the conduction electrons and by the inter-band transitions, and therefore the frequency ω_{min} corresponding to R_{min} is not equal to the plasma frequency ω_p. By separating the contribution from the conduction electrons (ε^e) (curve *4* of Fig. 6*b*) to the real part of the dielectric constant ε_1 (curve *1* of Fig. 6*b*) we can determine the true value of the plasma frequency ω_p. Inspection of the characteristic loss function ($-\mathrm{Im}\,\varepsilon^{-1}$, curve *3* of Fig. 6*b*) establishes the presence of a broad maximum at energies of 27–30 eV, due to the onset of plasma vibrations of the valence electrons. The calculated energy of these vibrations is 20 eV, i.e. we find (as in the case of the conduction electrons) a shift in the energy of the plasma vibrations as a result of band-to-band transitions. The similarity between the spectral dependence of the characteristic loss functions for LaB_6 and for the betarhombohedral modification of elemental boron suggests that the role of the boron atom in the formation of the spectrum of the hexaboride is dominant in the high-energy region.[76]

The boron sublattice of LaB_6 also determines the form of the Raman spectrum, which was studied on monocrystals prepared by zone melting.[56,77] The spectra were measured on polished (100) and (111) surfaces of monocrystals. Several peaks were observed, and assigned to three modes of lattice vibration active in the Raman region:

	From Ref.56	From Ref.77	
A_{1g}	1258 cm^{-1}	1262 cm^{-1}	B-B bond
E_g	1120 cm^{-1}	1138 cm^{-1}	B-B bond
F_{2g}	682 cm^{-1}	688 cm^{-1}	distortion of the boron sublattice

A peak at 214 cm^{-1}, attributed to scattering on defects of the crystal structure, was also observed.[77] A similar peak at 208 cm^{-1} was observed[58] in $La_{1-x}Ba_xB_6$ monocrystals (where $x = 0.02-0.046$) and attributed to the local perturbation of the symmetry produced by the replacement of La by Ba.

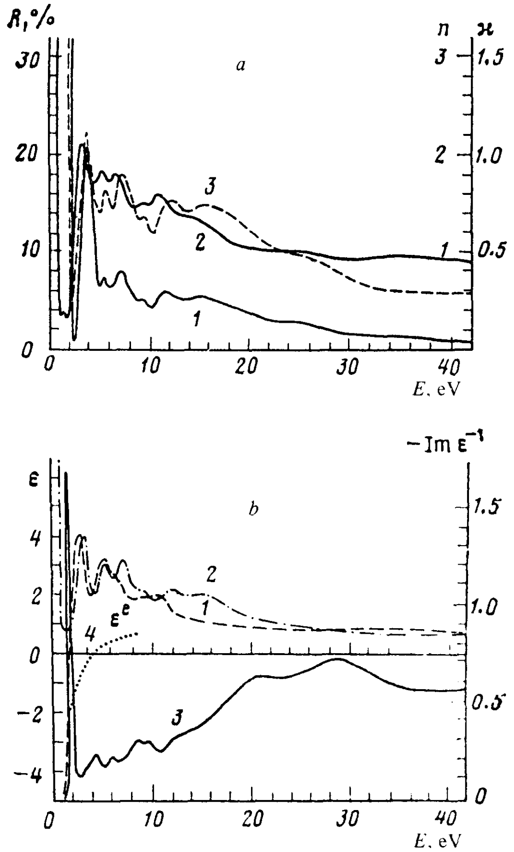

Figure 6. Dependence of the optical constants of LaB_6 on the energy *E* of the incident radiation;[75,76] *a*) reflectance *R* (*1*), refractive index *n* (*2*), and extinction coefficient κ (*3*); *b*) real (ε_1, *1*) and imaginary (ε_2, *2*) parts of the dielectric permeability function and of the loss function ($-\mathrm{Im}\,\varepsilon^{-1}$, 3).

3. Mechanical Properties

The elastic properties of LaB_6 are also determined mainly by the boron sublattice, as shown by measurements of the elastic constants of LaB_6 on samples cut in the <001>, <110>, and <111> directions from single crystals prepared by zone melting:[57]

$$C_{11} = 45.33 \times 10^{10}\ \mathrm{Pa}$$
$$C_{12} = 1.82 \times 10^{10}\ \mathrm{Pa}$$
$$C_{44} = 9.01 \times 10^{10}\ \mathrm{Pa}$$

The anisotropy factor is $A = 2C_{44}/(C_{11} - C_{12}) = 0.41$. Young's modulus, calculated for the <100> direction, is 45.18×10^{10} Pa, while the value calculated from the force constants of the bonds in the boron sublattice between octahedra and within the octahedra[56] is 40×10^{10} Pa. This good agreement is interpreted[57] as evidence that the elastic constants of LaB_6 are determined by the rigid boron sublattice. The large ionic contribution to the bond between the boron and the metal sublattice accounts for the anisotropy factor $A < 1$ in LaB_6 (a value usually found in ionic crystals).

Young's modulus for polycrystalline LaB_6 prepared by zone melting is 39.24×10^{10} Pa,[78] i.e. it is slightly lower than for the monocrystals. It is interesting to note that a theoretical calculation of Young's modulus for LaB_6 [79] gave a value of 47.09×10^{10} Pa, i.e. in these monocrystals the measured Young's modulus is very close to the theroretical value.

Data on the micro-hardness of LaB_6 monocrystals prepared by various methods are shown in Table 6. They cover a wide range, but since the measurements were carried out with different loads it is difficult to compare the results. There is an obvious tendency for the micro-hardness to decrease with increasing load on the indentor. Furthermore, the micro-hardness measured with a Vickers pyramid (H_V) is different from that measured with a Knoop pyramid (H_K), which is a characteristic of brittle materials.[80] The brittleness of LaB_6 is found to be similar to that of silicon.[80]

Table 6. Micro-hardness of LaB_6 monocrystals measured by different methods. •

Method of preparation; crystal form; face	Micro-hardness, kg mm^{-2}		Load on indentor, g	Refs.
	H_V	H_K		
Gas phase; needles; (100)	3400—3700	—	50	[26]
Solution; platelets, needles; (100)	2620±80	—	100	[42]
Liquid phase	2020	—	300	[21]
Liquid phase: (100)	—	1850±90	510	[80]
(110)	—	1550±60		[80]
(111)	—	1490±70		[80]
Solution: (100)	—	2450	50	[81]
ditto	—	1980±130	200	[81]
"	—	1720	400	[81]

The anisotropy of the micro-hardness has been studied on monocrystals prepared by zone melting[80] and by the solution method.[81] In a study[81] of the anisotropy of the hardness (polar anisotropy) on the (100) face the maximum hardness was found with the longer diagonal of the indentor oriented in the <010> direction, and the minimum in the <011> direction (the difference between the two measurements was 300 kgf mm^{-2}). Ref.80 describes a study of the reticular anisotropy of the micro-hardness, showing that the maximum value of H_K occurs in the (100) plane, where the density of La atoms is a maximum, and the minimum occurs in the (111) plane.

4. Emission Properties

Because of the extensive use of LaB_6 cathodes in various types of electronic device, data on the thermo-electronic work function ϕ of the material are of interest. The cathode current density I_c during thermo-electronic emission is described by the Richardson–Dushman equation

$$I_c, \text{A cm}^{-2} = AT^2 \exp(-e\varphi/kT) \quad (1)$$

where T is the temperature of the cathode (K), e is the charge on the electron, and A is the Richardson constant. The work function ϕ can be determined by two methods: 1) graphically, from the slope of the linear plot of $\lg(I/T^2)$ against e/kT (we shall call this value of the work function ϕ_R), and 2) by calculation from formula (1), assuming a value of the Richardson constant of $A = 120$ cm^{-2} K^{-2} (we shall call this value ϕ_{ef}). Both ϕ_R and ϕ_{ef} values are used in published work, though according to some workers[83] the use of ϕ_{ef} is preferable.

The results of various workers on the work function of polycrystalline LaB_6 and of LaB_6 monocrystals have recently been critically examined in Refs.83 and 84 respectively.

Storms and Mueller[83] examine in detail the various factors responsible for the large scatter of the measurements of work function on polycrystalline LaB_6: deviations from stoichiometry in the bulk of the sample, differences in composition of the surface whose emission is measured, the temperature of the experiment, and the hold time of the sample at this temperature, the presence of impurities in the sample and in the residual atmosphere, and many other factors. For polycrystalline samples of composition in the range $LaB_{5.85}$–$LaB_{6.50}$ the surface composition at 1500 K varied between $LaB_{6.032}$ and $LaB_{6.047}$, the work function ϕ_{ef} was 2.91–2.93 eV, and ϕ_R was 3.15–3.12 eV. Surprisingly, a further increase in the overall boron content produces an increase in ϕ_{ef} and a decrease in ϕ_R (a sample of composition $LaB_{8.6}$, with a surface composition $LaB_{6.1}$, gave $\phi_{ef} = 3.17$ and $\phi_R = 2.21$ eV).

Evidently, these factors must affect the measured work function also in the case of monocrystals. Furthermore, the work function of the LaB_6 sample depends on the crystallographic direction, as in metals with body-centred cubic, face-centred cubic, or close-packed hexagonal crystal lattice. Data on the emission properties of monocrystals prepared by liquid-phase and by solution methods are shown in Table 7. We note that the scatter in the ϕ values is large also in monocrystals. Nevertheless the anisotropy in the work function with respect to the crystal orientation is clearly observable: $\phi_{(100)} \leq \phi_{(110)} \leq \phi_{(111)}$.

Table 7. Work functions of different faces of LaB_6 monocrystals prepared by liquid-phase and solution methods.

(100)		(110)		(111)		Refs.
φ_R, eV	φ_{ef}, eV	φ_R, eV	φ_{ef}, eV	φ_R, eV	φ_{ef}, eV	
Liquid-phase method						
2.4±0.2	—	—	—	—	—	[85]
2.91	2,70	3.09	2.98	2.85	3.35	[21]
2.86±0.03	—	2.68±0.03	—	3.4±0.2	—	[86]
—	2.52±0.05	—	2.64±0.05	—	2.90±0.05	[84]
—	—	2.74	—	2.0	—	[87]
—	2.75	—	2.88	—	2.98	[31]
Solution method						
2.47±0.06	—	—	—	—	—	[36[
—	2.38	—	2.07	—	—	[37]
3	—	—	—	—	—	[88]
—	2.70±0.05	—	—	—	—	[89]
—	2.86±0.04	—	—	—	—	[52]
2.3±0.1	—	—	—	—	—	[90]

It would be interesting to compare the work functions of monocrystals differing in purity and in composition. Unfortunately, this comparison is possible only in a few cases because of the inadequate specification of the experimental materials in much of the published work. Thus, boron-rich crystals prepared by zone melting ($La_{1-x}B_6$) and having a high impurity concentration[21] have a higher work function (on all faces) than crystals with a boron deficit ($LaB_{5.86}$) containing very few impurities.[30,84] The work function of the (100) face of LaB_6 monocrystals[89,90] prepared by a solution method[37–39] and containing ~10^{-2} wt.% of impurity is close to that of crystals prepared by zone melting and having a similar impurity concentration.[21,31]

By using modern methods of studying solid surfaces such as Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) the effect of impurities on the work function of LaB_6 monocrystals has been demonstrated more clearly. In particular, it has been shown[91] that the carbon present in the sample prepared by zone melting with one zone pass diffuses to the surface on heating the sample and forms a monolayer of graphite which is stable for a long time even at 1500 K. This effect increases the work function of LaB_6.

It has been shown[84,90,92] that carbon and oxygen are the main impurities on the (100), (110), and (111) surfaces of LaB_6 monocrystals. Their bond to the surfaces is fairly strong, and they are completely removed only by heating the sample to ~1700 K in a vacuum of 10^{-8}–10^{-10} mmHg. Studies of the oxidation kinetics at room temperature of clean (100), (110), and (111) surfaces of LaB_6 monocrystals showed that at oxygen pressures of 10^{-7}–10^{-9} mmHg O_2 adsorption raises the work function of these faces by 1.6, 1.3, and 1.1 eV respectively.[92–96] Raising the temperature to 1700 K strengthens the oxidation, and produces an increase of 2.4 eV in the work function of the (100) face[92] and a decrease in the emission current.[90,91] A large decrease in emission current is produced also by hydrogen, methane, and water vapour.[90] It has been established that rearrangement of the (110) monocrystal surface with formation of (111) facets takes place in an oxygen atmosphere at ~10^{-6} mmHg and 1700 K, leading to an increase in the work function of the (110) face and a decrease in emission current.[86,98]

Table 8. Atomic ratio B/La on the surface of different faces of LaB_6 monocrystals prepared by solution and by liquid-phase methods.

Face	B/La	Measurement method	Refs.	Face	B/La	Measurement method	Refs.
Solution method				Liquid-phase method			
(100)	2.3—2.6	AES	[36]	(100)	4.1 ± 0.1	AES	[84]
(100)	2.33—2.60	AES	[92]	(100)	4.0	UPS	[101]
(100)	2.0	AES	[1]	(110)	5.4 ± 0.1	AES	[84]
				(111)	5.9 ± 0.2	AES	[84]

The nature of the work function anisotropy in different faces of the LaB_6 monocrystals is also of interest. Studies of these faces by AES, LEED, UPS (ultraviolet photoelectron spectroscopy), and XPS (X-ray photoelectron spectroscopy) have shown[36,84,87,92,93,99–101] that the Ba/La ratio on the monocrystal surface increases in the sequence (100) < (110) < (111) (see Table 8). The work function decreases in the same order, i.e. the greater the density of La atoms on the surface, the lower is the work function. This observation is unexpected, since the opposite effect is found on elemental metals: ϕ increases with the density of metal atoms on the surface. The explanation of this anomaly probably resides in the atomic structure of the surface in the different faces of the LaB_6 crystals.[102,103,106,112] According to current views, the (100) surface consists of a plane of La ions, whereas in the (110) and (111) faces the La ions are displaced from their equilibrium positions by ~1.66 and 1.2 Å respectively (Fig.7), i.e. the greater the displacement of the La ions "from within" towards the surface, the lower is the work function. According to some workers[100–103] the difference in work function of the LaB_6 faces is explained by differences in the electrical dipole moments created by the positively charged La^{3+} ions and the octahedra of B atoms in the surface layer: the work function of the (100) and (110) faces is lower than that of the (111) face because their dipole moment is higher.

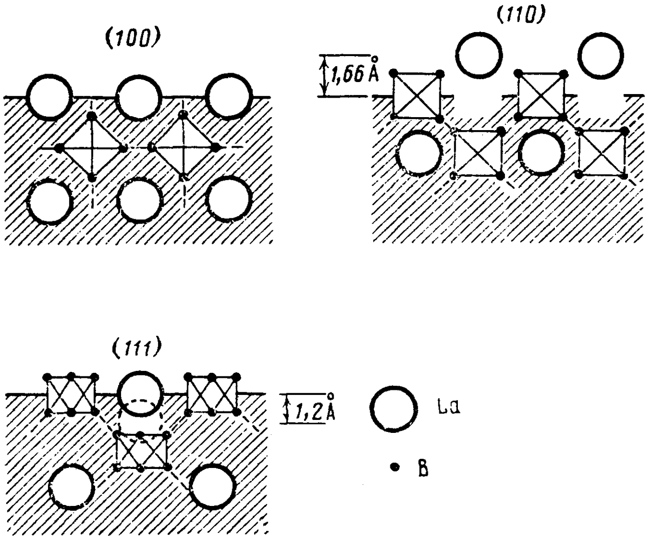

Figure 7. Surface structure of different faces of the LaB_6 crystal (from Ref.103).

Recent studies[104–106] of the energy structure of the LaB_6 surface have identified several peaks in the region of 1.5 to 3 eV below the Fermi level from the UPS spectra of the (100), (110), and (111) faces. These peaks are attributed to the so-called "dangling" bonds, i.e. to uncompensated bonds of the surface boron atoms.[107] The peaks disappear when oxygen is adsorbed on the LaB_6 surface, indicating an interaction between the oxygen atoms and the uncompensated boron bonds.[96] Adsorbed oxygen (or other gases) can form a dipolar surface layer which alters the surface potential and therefore also the work function.[94–96]

However, residual gases, including oxygen, can increase the emission rather than impair the emission properties.[108,109] Thus, it was found[109] that at an oxygen partial pressure of 10^{-10}–$(1-3) \times 10^{-9}$ mmHg the work function of the (210) face is ~0.2 eV lower than for the clean surface, and the emission is correspondingly higher. No explanation has yet been suggested.

Problems of adsorption on the surface of LaB_6 monocrystals are of practical as well as of theoretical interest in relation to the controlled modification of the emission characteristics by the simultaneous adsorption of several elements. For example, it has been shown[110] that the adsorption of Cs on the clean (100) and (110) faces of a LaB_6 crystal lowers the work function from 2.78 to 1.97 and 1.88 eV respectively. However, if the Cs is adsorbed on the same surfaces previously covered with oxygen the work function falls to 1.35 and 1.47 eV respectively. These surface coatings were found to have a reasonable thermal stability: thus, the Cs is desorbed from a clean

(100) surface of the LaB_6 crystal at ~900 K, whereas on a surface previously coated with oxygen desorption takes place at ~1150 K.[111] The work function of the clean (100) face may not be the lowest, of course. Higher-index faces have also given low values of the work function: $\phi_R = 2.3$ eV for the (321) face,[85] $\phi_{ef} = 2.41$ eV for (364),[84] $\phi = 2.2$ eV [112,113] and $\phi_R = 2.48$ eV for (210).[102]

Another method of improving the emission properties of LaB_6 monocrystals relies on doping the material. We know that the work function is given by the expression

$$\varphi=\chi-\mu \qquad (2)$$

where χ is the difference between the electrical potentials in the bulk of the metal and in the vacuum near the surface, and μ is the chemical potential of the electron gas in the metal ($\mu \approx E_F$, where E_F is the Fermi energy).[82] By varying χ or μ (for example, by doping) we can vary the work function of the LaB_6 in the required direction. In this respect the most promising materials are solid solutions based on LaB_6 in which some of the La atoms are replaced by other materials, especially rare-earth and alkaline-earth metals.

The emission properties of some solid solutions have been measured both on monocrystals and on polycrystalline samples.[51,52,88] It was found that the work function of the (100) face of the solid solution is higher than that of the LaB_6 crystals, and relatively insensitive to the nature of the added metal. It was also shown[52] that the surface of crystals of the LaB_6 solid solutions gradually become enriched in La (with respect to the bulk) at high temperatures as a result of the preferential evaporation of the second metallic component. These materials show a characteristic instability of the emission current.[88] Similar phenomena have been observed in polycrystalline solid solutions of the MB_6 type, where M = La, Y, Sc.[114] Nevertheless further work on these materials should be of interest.

Studies of field emission from LaB_6 monocrystals are also of great theoretical and practical interest in connection with the development of new materials for auto-emission cathodes.[115–117]

The first studies of field emission in an ion beam were carried out with monocrystals prepared by liquid-phase[115,118] and by solution methods.[119] It was shown that the image of a LaB_6 point in He ions at 78 K has an irregular structure. The quality of the image was worse than for metal points. However, later workers obtained images of LaB_6 points with a regular structure.

Studies of the effect of various gases (hydrogen,[120] neon, oxygen, and hydrogen[121]) on the image from a LaB_6 point revealed a rearrangement in a hydrogen atmosphere from low-index faces into faces with higher indices of the type of {012}, {013}, {112}, etc., whereas in the presence of oxygen the surface becomes strongly disordered, with cluster formation. The hydrogen reacts primarily with the surface B atoms,[120] and the oxygen with both the La and the B atoms.[121]

A study[122] of the mechanism of formation of images from points of LaB_6 and $La_{0.58}Sm_{0.42}B_6$ monocrystals in helium, neon, and hydrogen ions showed that only the metal ions (La or La and Sm) contribute to the formation of the image. However, others[121] assume that the main contribution to the formation of images of the points in He and Ne is from the uncompensated bonds of the boron atoms in the octahedra. This point of view is confirmed to some extent by studies of LaB_6 by the atomic probe method, with mass spectrometric analysis of the ions produced by field evaporation.[123,124]

Swanson[84] measured the work function and the field emission current of monocrystal points, and he concluded that LaB_6 has no real advantage as a field emitter over other refractory compounds. However, by generating microscopic projections on a point from a <100> LaB_6 monocrystal an emission current of ~10^{-5} A was obtained from the projection,[125] corresponding to a source brightness of ~10^{11} A cm^{-2} steradian^{-1}.

Nevertheless further studies of LaB_6 in an ion beam are of interest both from the standpoint of a more detailed understanding of the surface structure at the atomic level and to explain the mechanism of image formation from points of compounds. Furthermore it has been shown[102] that the evaporation under the influence of a field and the reconstruction of a surface can affect the concentration of La atoms, and therefore also the work function of the various faces. This work is extremely relevant, because using a thermo-emission cathode made of monocrystalline LaB_6 in an electron gun produces a spotty emission,[126,127] which can be eliminated (while at the same time increasing the brightness of the image) by operating the cathode in the thermal-field emission mode.[109]

5. *Some Practical Applications*

Because of the unique combination of physicochemical properties offered by LaB_6 its practical applications are extremely varied, and we shall only dwell on the most interesting and important results (in our opinion). The use of LaB_6 as a thermo-electronic emitter in the cathodes assemblies of various types of device should be mentioned first. The advantages of cathodes made of sintered LaB_6 over tungsten cathodes for use in scanning electron microscopes have long been recognised.[128–130]

The preparation of LaB_6 monocrystals stimulated the production of monocrystalline thermo-emission cathodes, the study of their characteristics, and the search for possible alternatives to oxide and tungsten cathodes.[88,106,118,126,131–143] The operating characteristics of a monocrystalline LaB_6 cathode used in commercial equipment (microanalysers and Auger spectrometers) in place of a tungsten cathode have been measured.[106,133,134] The LaB_6 cathode is shown to be brighter than the tungstem cathode (2×10^5 A cm^{-2} steradian^{-1} and 1.5×10^4 A cm^{-2} steradian^{-1} respectively), and to have a more stable emission current (better than 1×10^{-3} A h^{-1}). It was also shown[134] that a cathode consisting of a LaB_6 point with a <100> orientation can produce a cathode current density of ~50 A cm^{-2}, combined with an operating life of more than 300 h. An electron gun with a cathode made from a zone melted LaB_6 single crystal cut in the <100> direction has been developed,[135] giving an optimum brightness of 2.5×10^5 A cm^{-2} steradian^{-1} at a cathodic current density of 50 A cm^{-2}. A cathode with a monocrystal oriented in the <100> direction was reported[84] to give a current density of ~10 A cm^{-2} at 1600 to 1700 K; under these conditions the rate of evaporation of the cathode was ~1 μm year^{-1}.

The successful replacement of a rhenium cathode by a monocrystalline LaB_6 cathode in a commercial mass spectrometer has been claimed.[136] The life of the LaB_6 cathode is 10 times greater than that of the rhenium cathode, and its working temperature is lower (1750 K instead of 2500 K), which allows thermally unstable compounds to be analysed. The replacement[139] of a tungsten cathode in a micro-focus X-ray source by a LaB_6 monocrystal has given a 20 times higher current density at the target with an operational life of ~800 h.

A monocrystalline LaB_6 cathode has been fitted[140] to an electron microscope, giving a brightness of 2×10^6 A cm^{-2} steradian^{-1} and a stable operation time of over 100 h; the resolution of the microscope was 0.14 nm.

Another promising application of monocrystalline LaB_6 cathoodes is in the production of integrated circuits by electron-beam lithography.[138] A very precise and fast lithographic system has been based[141] on a monocrystalline LaB$_6$ cathode consisting of a flattened point, giving an electron beam 6.4 × 6.4 μm in cross-section and a current density of 10A cm^{-2}.

Work is also in progress on improved designs of cathode assemblies[142] and on optimised conditions for using the monocrystalline LaB$_6$ cathodes.[143] Thus a new method of attaching the monocrystal of lanthanum hexaboride to the cathode assembly gives a working life of 1000 h at a cathode working temperature of 1800 K.[142]

Considerable effort is devoted also to the use of polycrystalline LaB$_6$. For example, it has been shown that cathodes made from hot-pressed or sintered polycrystalline LaB$_6$ are potentially useful for high-current ion sources in atomic technology,[144-147] especially for the production of a high-density plasma in apparatus of the "Tokamak" type.[145,146] Sintered LaB$_6$–ZrB$_6$ compositions have also been studied with the aim of improving the mechanical and emission properties of LaB$_6$ cathodes.[148]

Powdered LaB$_6$ has been used in the isotopic analysis of iodine,[149] and found to give a relative sensitivity better than materials like the W–Th alloy, ZrC, Hf, and Re.

A study of the catalytic activity of the clean surface of LaB$_6$ powders towards the hydrogen–deuterium isotope exchange has been reported.[150] At 159 K the specific activity of LaB$_6$ is two orders of magnitude greater than the activity of γ-Al$_2$O$_3$, and only slightly lower than the activity of Pt or Ni.

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Thus the preparation of perfect monocrystals of LaB$_6$ by any of the methods examined requires accurate information on the La–B phase diagram, and in particular on the homogeneity region of LaB$_6$. Another important requirement is a very accurate characterisation of the resulting LaB$_6$ crystals in both composition and structure, to allow these data to be related to the other properties of the material. Only by establishing these relationships can the controlled production of perfect and defect-free LaB$_6$ monocrystals, by any method, be achieved.

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Electrochemical Behaviour of Phenols

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The literature data on the electrochemical behaviour of phenol and its adsorption on various anodic materials (platinum, graphite, gold, and lead dioxide) are surveyed and the influence of the rate of application of the potential, temperature, pH, the rate of rotation of the electrode (stirring) on the maximum oxidation current of phenol and its half-wave potential is examined. The present concept concerning the mechanism of the primary electrode reaction is analysed and the possibility of the extensive oxidation of phenol is considered. The influence of a series of substituents [OH, CH_3, NO_2, Cl, C_6H_4, COOH, C_2H_5, and $C(CH_3)_3$] on the principal characteristics of the potentiodynamic relations is examined and the possibility of a correlation between the half-wave potentials $E_{1/2}$ of substituted phenols and the Hammett constants is analysed.
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I. INTRODUCTION

In connection with wide scale industrial use of phenols, two problems have arisen: the development of convenient and selective methods for their analysis and the removal of phenols from the waste water in industrial undertakings. The latter is related to the high toxicity of phenols and the difficulty of decomposing them by the usual chemical means. Electrochemical methods, especially anodic oxidation, proved to be sufficiently effective for the solution of both problems, which is the reason for the increased interest of investigators in the electrochemistry of phenols.

The aim of the present review is to survey the factual data which have accumulated concerning the oxidation of phenols on anodes.

II. THE PLATINUM ELECTRODE

1. Potentiodynamic Measurements

There is a distinct oxidation wave on the voltage–current curve obtained in the oxidation of phenol on stationary and rotating platinum anodes. A typical form of such curves is illustrated in Fig.1. At a phenol concentration $c_{ph} < 1 \times 10^{-4}$ M under both stationary and dynamic conditions, a single wave is observed with a distinct limiting current and there is a linear relation between the limiting current and c_{ph}. At $c_{ph} > 1 \times 10^{-4}$ M, a decrease of the current is observed on the voltage–current curves, which is due to the inhibition of the electrochemical oxidation process and the linear relation between the maximum current and c_{ph} breaks down—the current increases more slowly than the concentration.[1-3]

It has been noted that during the measurement of the potentiodynamic relation, a readily visible yellow-brown polymeric product is formed on the anode. In order to investigate the kinetics of the growth of this polymer film, ellipsometric measurements have been made in the electrochemical oxidation of phenol in 0.5 M H_2SO_4 solution.[4] Optical studies have shown that, at low potentials (~1 V relative to the reversible hydrogen electrode in the same solution), the rate of growth of the film is low and its thickness is proportional to the square root of the electrochemical oxidation time. The rate of formation of the film increases sharply as the potential shifts towards high positive values (≥2 V) (Fig.2); under these conditions, its thickness reaches on average 1000–10 000 Å.

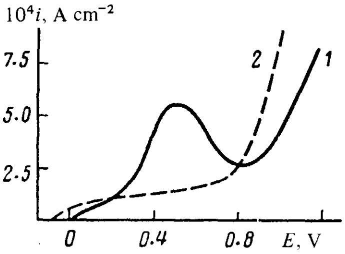

Figure 1. Potentiodynamic curve for phenol ($c_{ph} = 1 \times 10^{-3}$M) in a saturated borax solution at a platinum anode (i = current density; rate of application of potential $v = 40 \times 10^{-3}$ V s^{-1}; pH 9.5; 20 °C): *1*) supporting electrolyte plus phenol; *2*) supporting electrolyte.[3]

The observed decrease of the current on the potentiometric curve is in fact explained by the strong adsorption of the reaction products and the blocking by the latter of the anode surface.[1-3] Levina et al.[5], who investigated the electrochemical oxidation of phenol in 1 *N* H_2SO_4 solution, assumed that the decrease of the current is caused by the adsorption of oxygen, which cannot occupy the anode surface at low anodic potentials owing to the adsorption of phenol. Such competition for sites on the surface does indeed occur in the case of organic substances and must be taken into account.[6] However, in the study of the electrochemical oxidation of phenol in aqueous 1 *N* H_2SO_4 and NaOH solutions, the possibility of the formation on the anode surface of a film consisting not only of polymer molecules strongly bound to the surface but also of soluble products has been considered.[7,8] It has been suggested that, at low (<0.2 M) and higher concentrations, products of the second and first types predominate respectively.

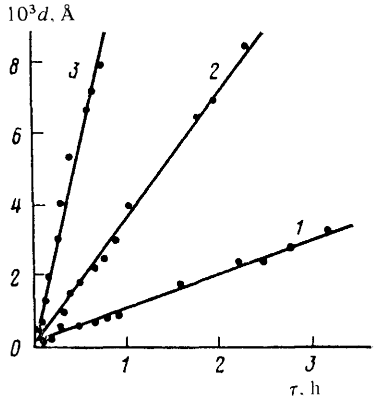

Figure 2. The rate of growth of the polymer film on the platinum electrode (d = thickness of film, τ = time) at three different potentials in a 0.5 M H_2SO_4 + 0.1 M C_6H_5OH solution; potential (V): *1*) 2.08; *2*) 2.15; *3*) 2.28.[4]

Judging from the shapes of the potentiodynamic curves, which have a deep minimum, the process should have ceased in the passivation region as the polymer film grew. Furthermore, it is well known that benzoquinone can be obtained in a satisfactory yield by the preparative oxidation of phenol. It has been suggested[8] that the oxidation of phenol in the passivation region requires that a barrier be overcome, the barrier consisting of the adsorbed polymer film. This phenomenon, involving charged transfer to the adsorbed film, is well known in polarography (the Loshkarev effect†) and involves the electrochemical reaction of a substance which has diffused towards the anode through the adsorbed layer which inhibits the process. In the case of phenol yet another explanation of the process under the conditions of the complete surfave coverage of the polymer film is possible: benzoquinone is formed on oxidation of the polymeric substance and phenol molecules are used to renew this polymer film.

The observed oxidation current depends to a large extent on the state of the surface of the anode, so that identical preliminary treatment of the electrode surface is necessary in order to obtain reproducible results. A positive effect of heat treatment[2] and of electrochemical treatment[1,3] on the surface has been noted. There is no unanimous view concerning the problem of the ratio of the maximum currents on the oxidised and reduced platinum surfaces.[1,7,11]

With increase of pH to 9.0, the oxidation half-wave potential $E_{1/2}$ shifts towards less positive values and, on further increase of pH, remains almost constant.[2] Although the $E_{1/2}$ for irreversible processes lacks the thermodynamic significance of the half-wave potential for reversible processes, its variation nevertheless provides an idea about the range of potentials in which the electrochemical process takes place. The observed shift of the phenol oxidation potential when the pH changes by unity is ~60 mV.[3]

It has been stated that the maximum phenol oxidation current depends on the pH of the medium.[2,3,5,12] However, the published data are exceptionally contradictory. Thus an appreciable change in the maximum oxidation current at pH from 5.0 to 11.0 has not been noted by Hedenburg and Freiser,[2] or Kharlamova et al.[3] and Levina et al.[5] observed in a neutral medium a decrease of the maximum phenol oxidation current compared with the currents in acid and alkaline media, while Zeigerson and Gileadi[12] altogether failed to observe the phenol oxidation current in acid and neutral solutions. They explained[12] the lack of the current by the fact that two reactions take place on the clean electrode surface—the oxidation of phenol and the formation of a layer of adsorbed phenoxy-radicals, and, as soon as the degree of surface coverage approaches unity, the rates of both reactions fall to zero, i.e. complete passivation of the process takes place. Passivation is observed at a fully determined potential, which depends on the concentration of the substance and the pH. In this connection, we may recall that phenol may be oxidised also in the passive region (see above). Evidently the authors[12] did not note the small difference between the supporting electrolyte current and the current in the presence of phenol.

The maximum current is influenced by the rate of application of the potential ν: with its increase, the maximum current rises and the rate of increase depends on the initial phenol concentration. An increase in the rate of application of the potential hardly affects the $E_{1/2}$ for the oxidation of phenol.[1]

An increase in the solution temperature (from 20° to 60 °C) entails a rise in the maximum phenol oxidation current. The temperature coefficient in an aqueous buffer solution is 2.5 to 2.9% per degree,[1,3] which may indicate a non-diffusional nature of the maximum current.

The results examined show that, for a correct interpretation of the anodic process, it is essential to possess quantitative data for the adsorption of phenol on the electrode at different potentials.

2. Adsorption

The dependence of the degree of electrode surface coverage by phenol in 0.1 *N* H_2SO_4 solution on the potential (in the range from −0.3 to +1.0 V) has been determined by the potentiodynamic pulse method (Fig.3).[13] In an analogous solution and in the same range of potentials an extremely weak dependence of the degree of adsorption on the potential in the range from −0.1 to +0.4 V [relative to the normal hydrogen electrode (n.h.e.)] has been found, in agreement with Levina et al.[13], and is described by the Temkin isotherm.[14] According to Levina et al.[13] and Kazarinov et al.[14], the adsorption kinetics obey the Roginskii–Zel'dovich equation.

The dependence of the degree of adsorption of phenol on the potential at different pH has been determined with the aid of rapid galvanostatic pulses taking into account the surface roughness factor and the amount of adsorbed oxygen.[3] It follows from Fig.4 that the degree of adsorption of phenol

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†M.A.Loshkarev and Yu.M.Loshkarev, in "Vol'tamperometriya Organicheskikh i Neorganicheskikh Soedinenii" (Voltage–Current Measurements for Organic and Inorganic Compounds), Izd.Nauka, Moscow, 1985, p.35.

on the anode is almost independent of pH. If it is supposed that phenol is oxidised to CO_2 and H_2O, i.e. that the number of electrons involved in the reaction is $n = 28$, then the degree of adsorption per unit true surface is 4×10^{-10} mol cm^{-2}, which agrees with the data of Kazarinov et al.[14]

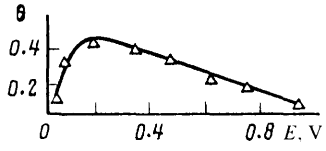


Figure 3. Dependence of the standard surface coverage of the platinum electrode θ in a 1×10^{-4} M solution of phenol on the electrode potential in 0.1 *N* H_2SO_4 solution (the potentials were measured relative to the reversible hydrogen electrode in the same solution).[13]

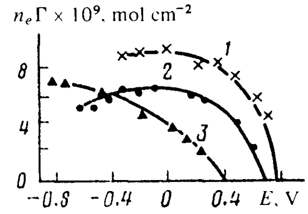


Figure 4. Dependence of the adsorption of phenol (from a 1×10^{-3} M solution) on the platinum anode on the potential at pH 1.6 (curve *1*), 7.5 (curve *2*), and 9.5 (curve *3*) taking into account the roughness factor and the amount of adsorbed oxygen (the potentials were measured relative to the 0.1 *N* calomel electrode) (n_e is the number of electrons involved in the process).[3]

Chronopotentiometric measurements in 0.1 *N* NaOH solution in the presence of 0.05, 0.1, and 0.4 M phenol[8] have shown that the amount of electricity corresponding to the transition time (i.e. the time during which a stationary current is established) falls with increase of the current and reaches a limiting value of 27.2×10^{-3} C cm^{-2} at the high polarising current density of 6×10^{-2} A cm^{-2}. In this case diffusion does not affect the transition time. During this period, the charging process takes place, the amount of charge generated exceeding by a factor of ~60 that necessary for the monolayer coverage of the platinum surface with oxygen. Hence it is concluded that the current is consumed in the formation of polymolecular phenol adsorption layers.

There exist data concerning the adsorption of a substituted phenol (*p*-nitrophenol) on the platinum anode at high anodic potentials (>1.0 V).[15] The dependence of the degree of adsorption of *p*-nitrophenol on the potential, obtained on platinised platinum in 0.1 *N* $HClO_4$ solution by the radioactive tracer method, shows that, starting from 1.3 V, the degree of adsorption rises sharply. This has been explained by the formation of a monolayer in the potential range 0.1 to 0.2 V and the fact that a polymolecular adsorbate layer is produced at $E > 1.0$ V. In determining the intensity of the UV spectra of *p*-nitrophenol and the adsorbed species, the authors[15] calculated the degree of adsorption of *p*-nitrophenol at high anodic potentials taking into account the areas of the electrodes. It was found that it corresponds to the formation of more than 10 adsorbate monolayers. However, judging from the potentiodynamic curve, the inhibition of the phenol oxidation process in acid aqueous solutions begins at a potential of ~1.0 V. For this reason, one cannot rule out the possibility that the observed multilayer adsorption refers not to phenol but to its oxidation product (see above).

Data concerning the influence of chloride ions on the adsorption of phenol are contradictory. It has been stated[16] that phenol is adsorbed more effectively than chloride ions at a concentration of the latter of 0.1 V, but the phenol concentration has not been reported. It follows from the results of an investigation[17] that in 0.1 *N* H_2SO_4 solution the adsorption of phenol (1×10^{-4} M) and the chloride ions (0.1 M) is competitive. The decrease of the degree of adsorption of phenol (1×10^{-3} M) in the presence of chlorides (0.1 M), observed by Kharlamova et al.[3], can also be accounted for by competitive adsorption. Since all the experimental data presented have been determined under different conditions, one cannot obtain a clear idea about the influence of the concentration of chloride ions on the adsorption of phenol.

III. THE GRAPHITE ELECTRODE

1. Potentiodynamic Measurements

On the graphite anode (under stationary and dynamic conditions) in the concentration range 10^{-3}–10^{-6} M, phenol gives rise to a single wave on the voltage–current curve, as on the platinum anode. The phenol oxidation current is greatly influenced by the type of impregnation mass, which, by filling the graphite pores, ensured a constant current density throughout the anode surface.[18,19] A mixture of paraffin with polyethylene is usually employed for impregnation.

The published data make it possible to establish characteristics of the influence of individual factors (the concentration of the substance, the pH of the medium, the rate of rotation of the electrode, etc.) and the appearance of a maximum on the voltage–current phenol oxidation curve. By analogy with the platinum anode, one may expect that the maximum (decrease of the current) will be shown at a specific concentration of the test substance and it does indeed follow from a series of publications[20–22] that, at $c_{pH} = 10^{-4}$ M under stationary conditions, a distinct limiting current is observed, while at $c_{ph} = 10^{-3}$ M there is a maximum. However, the opposite behaviour has also been noted:[23,24] at $c_{ph} = 10^{-4}$ M a maximum was observed, while on raising the concentration to 10^{-2} M and above there was a distinct limiting current. Kharlamova et al.[3] observed a maximum only in 0.1 *N* H_2SO_4 solution at $c_{ph} = 10^{-3}$ M, while in neutral and weakly alkaline medium a distinct limiting current was noted. The appearance of a maximum was probably due to an additional factor which had not been taken into account.

At $c_{ph} \leq 10^{-4}$ M a linear dependence of the maximum current on the phenol concentration is observed, but at $c_{ph} > 10^{-4}$ M the linearity breaks down and the limiting current increases more slowly than the concentration.[20,23,25]

The state of the graphite surface, like that of the platinum anode, influences significantly the phenol oxidation current and a preliminary treatment of the electrode surface is therefore also necessary in this instance. In almost all the published studies the working electrode surface was treated mechanically (with emery paper, an aqueous suspension of alumina, etc.) before recording each potentiodynamic curve. The favourable influence of a two-stage electrode treatment has been noted: brief boiling in ethanol (0.5 min) followed by anodic treatment at the hydrogen evolution potential in 0.1 *N* H_2SO_4 solution for 2–3 min.[3] If the electrode is not treated again after recording one voltage–current curve, then in the repeated experiment two waves appear on the curve.[21]

The phenol oxidation current depends markedly on the pH of the medium, but, as for the platinum anode, the available data differ greatly. Thus the dependence of the maximum current on the pH was found to have a minimum in a neutral medium,[3,26] which can be explained by a decrease of the concentration of the unionised form of phenol. However, in another study[16] a maximum current was observed at pH 1.2, the current diminishing with increase of pH to 3.2, while on a further increase of the pH it remains almost unchanged. Another investigation established[3,27] that the current in an acid medium is higher than in an alkaline medium, on average by ~40%, while in the study of Korshunov et al.[28] the increment in the same pH range was found to be only ~3%.

The rate of application of the potential influences the maximum current. With increase of v by a factor of 2 (from 0.62 to 1.24 mV s^{-1}), the current rises, according to Gaylor and co-workers,[20,21] by a factor of 1.5–1.7, which is much greater than could be expected if the current were controlled by diffusion (it would then have increased by a factor of $2^{1/2}$). In our view, this can most probably be accounted for by the diminution of the role of passivating factors with increase of v, i.e. with decrease of the surface coverage by the polymeric substances.

An increase of temperature (from 20° to 60 °C) entails an increase of the oxidation current. The temperature coefficient in aqueous buffer solution is 0.4% according to Gaylor et al.[20], while according to other data[3,25] it amounts to 1.5–2.0% per degree.

Table 1. The influence of the pH on the half-wave potential for the oxidation of phenol ($E_{1/2}$, V) (relative to the saturated calomel electrode).

pH 1.2	pH 5.6	pH 7.0	pH 8.5	pH 9.0	Refs.
0.93	0.66	0.56	0.55	0.45	[20]
—	0.63	—	—	—	[22]
0.92	—	0.60	—	0.45	[23]
1.05	0.70	0.60	0.60	0.46	[26]

The half-wave potential decreases linearly with increasing pH until the latter reaches the p*K* of phenol, i.e. 9.89. A further increase of the pH does not induce a significant alteration of the half-wave potential.[3,25,26,29–31] Since $E_{1/2}$ for the oxidation of phenol is independent of the composition of the impregnation mass,[15] it is possible to compare its values at different pH obtained by different workers. Table 1 shows that the data agree well with one another.

An increase in the rate of application of the potential leads to a shift of $E_{1/2}$ towards positive potentials.[20]

There are data showing that $E_{1/2}$ is influenced by the phenol concentration. For example, a change in the phenol concentration by a factor of 10 results in a shift of $E_{1/2}$ by 22 mV at pH 5.2.[7,20]

2. Adsorption

The characteristics of the adsorption of phenol on the graphite anode per unit apparent surface at pH from 1.6 to 9.5 have been determined and its degree calculated.[3] Fig.5 shows that the degree of adsorption changes only slightly as the pH is altered.

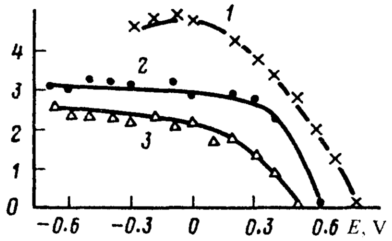


Figure 5. Dependence of the adsorption of phenol (from a 1×10^{-3} M solution) on the graphite anode on the potential at pH 1.6 (curve *1*), 7.5 (curve *2*), and 9.5 (curve *3*) (the potentials were measured relative to the 0.1 *N* calomel electrode).[3]

Comparison of the adsorption and potentiodynamic relations obtained on anodes of the same material has shown that the degree of adsorption of phenol begins to fall at the potential corresponding to the onset of its oxidation and almost ceases when the potential reaches the value corresponding to the maximum rate of oxidation. This is valid for both graphite and platinum anodes.[3]

IV. THE LEAD DIOXIDE AND GOLD ANODES

The electrochemical oxidation of phenol has also been investigated on lead dioxide[32,33] and gold[30] anodes.

On the stationary and rotating lead dioxide anodes in the presence of 0.5 M phenol in sulphuric acid solutions, a distinct anodic wave with a maximum is observed. The inhibition of the anodic process can be explained both by the blocking of the surface by the polymer film[32] and by the adsorption of oxygen.[33] It has been noted that at high positive potentials the film dissolves with the simultaneous evolution of oxygen. This phenomenon, which has not been observed on the platinum electrode (see above), can be evidence in support of the hypothesis that the mechanisms of the oxidation of phenol on platinum and lead dioxide are different.

In order to obtain reproducible results, before recording each anodic curve, the electrode surface was subjected to a preliminary treatment—anodic polarisation at E = +0.8 V [relative to the saturated calomel electrode (s.c.e.)] for 2–10 min.[32] The pH dependence of the oxidation current was investigated for a 0.5 M phenol solution in sulphuric acid at different concentrations (0.5–5 M H_2SO_4).[32] A shift of the current–potential curves of ~250 mV when the pH was altered by unity was then observed. This exceeds by a factor of ~4 the analogous value for the platinum and graphite anodes, which confirms the hypothesis that the phenol oxidation mechanism is different on lead dioxide.

On the gold anode in a solution having the composition $mNa_2SO_4 + nH_2SO_4$, phenol gives rise to a distinct oxidation wave with a maximum. In the pH range 1–14, the dependence of the change in the phenol oxidation half-wave potential on the pH is identical with the dependence obtained for the graphite anode.[30]

V. THE MECHANISM OF THE ANODIC PROCESS

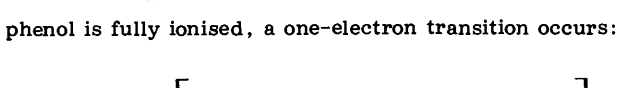
A considerable number of studies devoted to the phenol oxidation mechanism have been published. There exist two sets of views at the present time concerning the mechanism of the primary electrode reaction.[11]

The supporters of the first view believe that the initial stage involves the loss of one electron and the formation of the phenoxy-radical. Calculation based on the dependence of $\lg[I/(I_d - I)]$ on the potential, where I is the instantaneous current and I_d the diffusion current, has shown that the anodic wave corresponds to the transport of one electron.[2] This result apparently refers to a phenol concentration $\leq 1 \times 10^{-4}$ M. However, it is not clear from the above study[2] for which pH the calculation has been carried out. Other evidence in support of the hypothesis that the current is diffusion controlled, apart from the proportionality of the current to the phenol concentration, is not presented in the above publication. However, such a dependence can be observed also for first-order reactions occurring in the kinetic region.

The number of electrons transferred has also been calculated[1] from potentiodynamic curves using the equation relating the electrode potential to the diffusion current. The calculation was performed for a solution with a phenol concentration of 1×10^{-4} M at pH 10.

The supporters of the second view believe that two electrons are transferred in the first oxidation stage and that an intermediate is formed.[21] On the basis of the proportionality of the current to the phenol concentration, it has been concluded that the current is diffusional. These data[21] refer solely to pH 5.2; the range of phenol concentrations employed is not indicated.

It has been shown[11] that the stoichiometry of the phenol oxidation process depends on the pH of the solution. The reaction mechanism has been studied in detail in acetonitrile solution and the results and conclusions have been tested in aqueous buffer solutions. The behaviour of phenol in solution in acetonitrile and water proved to be identical. Thus the oxidation of phenol in an alkaline medium is lower by a factor of ~2 than in an acid medium, which suggests that, in the systems where phenol exists in an unionised state, a two-electron process takes place:



If phenol is fully ionised, a one-electron transition occurs:

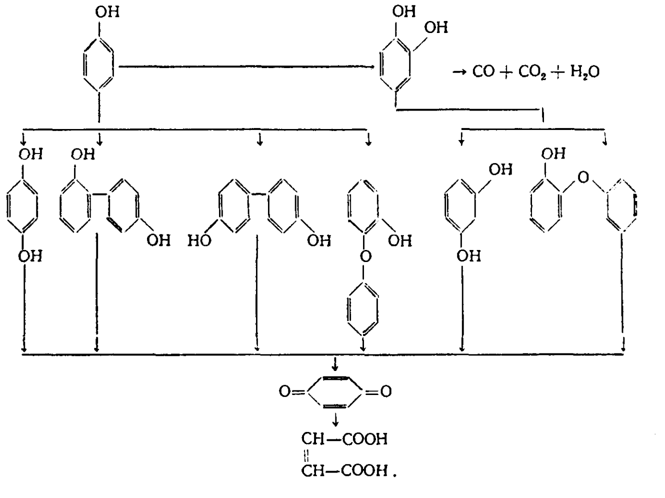
Later publications confirmed the existence of different views on the primary electrode process. In one of them it has been suggested that one hydrogen ion and one electron are involved in the electrode reaction.[26] In another communication[28] it is shown with the aid of the equation for the rotating disc electrode and potentiodynamic relations obtained on the graphite anode in buffer solutions (pH 1–12) that one electron is involved in the phenol oxidation reaction.

However, one should note that the diffusion coefficient was calculated[28] from the Stokes–Einstein equation. The quantity $n = 1$ was obtained for the phenol diffusion coefficient $D = 0.23 \times 10^{-5}$ cm^2 s^{-1}. Since the approximate character of the Stokes–Einstein equation is well known, the value of n calculated in the above study[28] must be treated with caution. Other factors giving rise to doubts about the validity of the calculations in the above investigation should also be noted. Firstly, it is known that the calculations of n and D from the equation for the rotating disc electrode can be performed only in the diffusion region. Furthermore, the above measurements[28] were performed at a single rate of rotation of the disc electrode, which makes it impossible to check in which region the study had been carried out. The conclusion that the measured current is determined by the rate of diffusion was reached solely on the basis of the satisfactory reproducibility of the product $i \cdot \tau^{1/2}$ obtained from chronopotentiometric data for the stationary electrode. Secondly, it has been shown[3] that the electrochemical oxidation of phenol at a concentration of 1×10^{-3} M in acid solutions is partly limited by diffusion, while in an alkaline solution the current is determined by the process kinetics alone. Naturally, in both cases the rotating disc electrode equation is unsuitable for the calculation of n.

The authors[28] were able to observe directly the EPR spectra characteristic of the phenoxy-radicals formed in the first phenol oxidation stage in acid, alkaline, and neutral media.

The mechanism proposed by Gaylor et al.[21] involves the transfer of one electron and one proton in the potential-determining stage and the formation of the $PhO^{\bullet}$ radical. On the other hand, other investigators[7,8,29] confirmed the dependence of the stoichiometry of the oxidation reaction on the pH of the solution observed by Vermillion and Pearl.[11]

It has been shown[34–36] that the first phenol oxidation stage is followed by the formation of unstable products, which enter into subsequent chemical reactions. The nature of these intermediates has not been discussed, but it can be inferred by analysing the final electrolysis products. It has been established that the electrochemical oxidation of phenol is a multistage process, which can be represented by the following scheme:[34–36]



The formation of hydroquinone and *pp'*-biphenol has been demonstrated by cyclic voltage–current measurements in 25% acetone solution in a Britton–Robinson buffer at a rate of application of the potential of 8.33 V min^{-1}.[35] In the oxidation of phenol in 0.05 M HCl solution (at pH 1.3, $\nu = 0.1$ V s^{-1}, $c_{\mathrm{ph}} = 1 \times 10^{-3}$ M) the formation of five reaction products was observed by the same method: *op*- and *pp'*-biphenols, hydroquinone, catechol, and hydroxyhydroquinone.[29] It was shown that all the products are formed as a result of the dimerisation of phenoxy-radicals obtained in the primary one-electron step.

The following mechanism of the total oxidation of phenol on the platinum anode in acid and alkaline media has been proposed:[6,8]

In an alkaline medium	In an acid medium
$\mathrm{PhOH} + \mathrm{OH}^- \rightleftarrows \mathrm{PhO}^- + \mathrm{H_2O}$	$\mathrm{PhOH} \rightleftarrows \mathrm{PhO}^{\cdot} + \mathrm{H}^+ + \bar{e}$
$\mathrm{PhO}^- \rightarrow \mathrm{PhO}^{\cdot} + \bar{e}$	$\mathrm{PhO}^{\cdot} + \mathrm{PhOH} \rightarrow \mathrm{P}_1^{\cdot} + \mathrm{H}^+ + \bar{e}$
$\mathrm{PhO}^{\cdot} + \mathrm{PhO}^- \rightarrow \mathrm{IP} + \bar{e}$	$\mathrm{P}_1^{\cdot} + \mathrm{PhOH} \rightarrow \mathrm{P}_2$
$\mathrm{IP} \rightarrow \text{products} + n\bar{e}$	$\mathrm{PhO}^{\cdot} + \mathrm{PtOH} + \mathrm{H}^+ \rightarrow \text{hydroquinone}$
	$\text{hydroquinone} \rightarrow \text{benzoquinone} + 2\mathrm{H} + 2\bar{e}$

Here $\mathrm{P_1}$ and $\mathrm{P_2}$ are dimers and trimers respectively and IP are intermediate products.

Determinations of the total number of electrons participating in the extensive oxidation of phenol under different conditions have been carried out in a series of studies. The study of the adsorption of phenol on the platinum anode (see Section II) at potentials below that corresponding to the onset of oxidation has shown[13] that phenol hinders the adsorption of oxygen when an anodic pulse is applied and the adsorption of hydrogen when a cathodic pulse is applied. From these data and also taking into account the fact that phenol gives rise to a distinct oxidation wave at positive potentials, the authors postulated the presence on the electrode surface of chemisorbed species of one type whose oxidation requires 4 ± 0.5 electrons. This number of electrons is determined by the fact that phenol is oxidised to $\mathrm{CO_2}$ and in this case 4.6 electrons correspond to each adsorption centre. Since the adsorption of phenol is accompanied neither by dehydrogenation nor electron transfer, the authors suggested that it occurs as a result of the dissociation of the double bonds in the benzene ring and the formation of six Pt–C bonds. In this case the plane of the aromatic ring should apparently be arranged parallel to the electrode surface. At the same time, Izumi et al.[8] and Bjerano et al.[37], who support the radical mechanism, suggest that the phenoxy-radical is adsorbed via the oxygen atom, so that the plane of the aromatic ring is more likely to be arranged at an angle with respect to the surface than parallel to it.

It has been suggested that the total number of electrons participating in the oxidation of one phenol molecule varies as a function of the rate of application of the potential from 3 (for $\nu < 1$ V s^{-1}) to 1.5 (for $\nu > 5$ V s^{-1}).[25] It has been found,[25] by means of calculation with the aid of the theoretical equation for the limiting diffusion current, that $n = 3$. The phenol concentration was then 10^{-6}–10^{-7} M and the dependence of the limiting current on the phenol concentration was linear at a flow rate of the solution relative to the electrode of 1×10^{-4} litre s^{-1}.

The influence of the rate of rotation of the electrode (or of the flow rate of the solution) on the maximum phenol oxidation current have been investigated in a number of studies and it has been shown that in an alkaline medium an increase of the rate of rotation of the platinum wire to 1000 rev^{-1} entails a steady increase of the maximum current.[1] However, it is known that the most reliable principal kinetic characteristics can be obtained with the aid of the rotating disc electrode. For this reason, a detailed study has been made[3] of the influence of the rate of rotation of the electrode on the phenol oxidation current on platinum and graphite disc anodes at different pH of the solution. The graphical method was used to calculate the order of the reaction.[38] Using the true kinetic current and the dependence of the oxidation current on the rate of rotation of the electrode, the authors[3] found that in acid and neutral media the oxidation of phenol (at $c_{\mathrm{ph}} = 1 \times 10^{-3}$ M) formally obeys a first-order equation. In an alkaline medium (saturated borate buffer solution, pH 9.5) the maximum phenol oxidation current remains constant when the rate of rotation of the platinum anode is raised from 160 to 4000 rev min^{-1}, which formally indicates a zero reaction order. The authors attribute this factor[3] to the formation of a strongly adsorbed polymer film on the electrode.

A dependence of the reaction order *P* on the initial phenol concentration in the solution has been observed.[8] The values of $P = (\partial\, \mathrm{ig}i/\partial\, \mathrm{lg}c_{\mathrm{ph}})_e$ were found experimentally at different concentrations in aqueous alkaline solutions (1 *N* NaOH solution) of phenol. It was shown that the order of the reaction is two at $c_{\mathrm{ph}} = 0.1$–0.5 M, while at lower concentrations it approaches unity, which is inconsistent with the data of Kharlamova et al.[3]

High reaction orders have been obtained by Levina et al.[5] Calculation of the order of the reaction on a smooth platinum electrode by the equation $i = kc_{\mathrm{ph}}^P$, where $P = 2.8$–3.0 showed that *P* is almost independent of the potential. The authors[5] attribute the anomalously high reaction orders to the anomalous adsorption properties of phenol at fairly high concentrations in solution (from 0.4 to 2 M). Furthermore, it has been noted that, in contrast to the isotherms obtained at potentials such that the oxidation of phenol does not yet occur, the adsorption isotherms in the range of oxidation potentials have a complex character. The degree of surface coverage initially increases slowly with increase of the phenol concentration, in conformity with the Temkin isotherm. However, after the attainment of the critical phenol concentration (~0.4 M), the surface is rapidly filled by chemisorbed species and the slope of the isotherm changes sharply. It has been suggested that this effect is caused by the surface condensation or heterogeneous polymerisation of phenol molecules.

From our point of view, this explanation conflicts with the known electrochemical properties of phenol. In particular, in the range of concentrations employed by Levina et al.[5], polymer layers on the anode surface can be observed even visually. For this reason, the isotherm apparently actually corresponds to the adsorption of not phenol molecules or their fragments but of the polymeric product. The break point then corresponds to the concentration at which polymerisation is particularly vigorous.

The discrepancies between the calculated reaction orders are probably associated with the fact that the authors measured not the true phenol oxidation current but the current distorted by the adsorption of the incomplete oxidation product. For this reason, the reaction orders indicated above are more likely to be purely formal quantities and therefore do not necessarily reflect the real process mechanism.

The maximum phenol oxidation current on the graphite anode in a buffer solution at pH 4.0 and $c_{\mathrm{ph}} = 5 \times 10^{-7}$ M is proportional to the rate of movement of the solution *u* raised to the power 3/4 [$u = (2.1$–$10.5) \times 10^{-5}$ litre s^{-1}].[39] With increase of phenol concentration, a deviation from this relation is observed, which can also be accounted for by the coverage of the surface of the anode by the reaction product.

Levina et al.[5] examined the question of the possible slow stage in the phenol oxidation process. Direct measurement of the rate of adsorption of phenol showed that it exceeds greatly the rate of the electrochemical oxidation and hence cannot be the slow stage.

As shown above (Section II), the half-wave potential for the oxidation of phenol shifts towards more negative values by ~60 mV per pH unit as the pH increases to 9.0. This suggests that the slow stage in the oxidation of phenol in 0.1 *N* H_2SO_4 solution on platinum is the interaction of OH^-_{ads} with the chemisorbed organic species.[5]

The mechanism of the oxidation of phenol on the lead dioxide anode is different from that on platinum and graphite. It has been noted that the phenol oxidation potential is close to the lead dioxide formation potential in these solutions.[32] This observation served as a basis for a new phenol oxidation mechanism on the lead dioxide electrode, according to which the potential-determining stage is the chemical oxidation of phenol by lead dioxide. The latter is regenerated in the electrochemical process, which requires the transfer of four electrons.[33]

VI. THE INFLUENCE OF SUBSTITUENTS ON THE ELECTROCHEMICAL ACTIVITY

We shall consider the influence of the OH, CH_3, NO_2, NH_2, Cl, C_6H_4, COOH, C_2H_5, and $C(CH_3)_3$ groups substituting hydrogen atoms in the benzene ring on the principal voltage–current characteristics of the oxidation of phenol.

1. The Platinum Anode

The influence of the hydroxy-group in the *m*-, *o*-, and *p*-positions in the benzene ring of phenol on the oxidation current in acid and alkaline aqueous media has been investigated[12] and, as noted previously (Section II), appreciable oxidation of phenol in an acid medium (1 M $HClO_4$ solution) was not observed in this investigation. Resorcinol (1,3-dihydroxybenzene) behaves analogously. However, the introduction of the hydroxy-group in the *o*- and *p*-positions renders the corresponding phenols (catechol and hydroquinone) readily oxidisable. The reversible oxidation of hydroquinone, which proceeds at an extremely high rate, is well known.[40] Catechol is apparently also oxidised reversibly. In an alkaline medium (1 M KOH solution), all three substituted phenols are oxidised, giving rise to maxima on the voltage–current relation. The maximum oxidation currents diminish in the sequence hydroquinone > catechol > resorcinol.

As stated above (see Section II), the appearance of a maximum on the voltage–current curve depends not only on the initial concentration of the corresponding phenol but also on the pH of the medium. This is illustrated by the oxidation of hydroquinone in a strongly acid medium (1 M $HClO_4$):[12] the anodic wave with a maximum appears only at a phenol concentration ≥0.2 M and, when the pH is raised to 3.0, the above concentration falls to 0.1 M. It is also noteworthy that the electrochemical oxidation of resorcinol on the anode surface results in the formation of an insoluble polymeric product, as in the case of phenol.[12]

The maximum resorcinol oxidation current increases with increasing pH, but to a much lesser extent than in the oxidation of phenol. When the pH is raised from 12.0 to 13.7, the increase in the maximum resorcinol oxidation current is ~100 times smaller than for phenol.[12]

The introduction of two hydroxy-groups into the phenol molecule in the 2,3- and 2,4-positions permits the oxidation of the resulting compounds in an acid medium and the maximum 2,4-trihydroxybenzene oxidation current is lower by ~30% than for the 2,3-analogue. In contrast to these compounds, 3,5-dihydroxybenzene is not appreciably oxidised in an acid medium, like the initial phenol. However, it is readily oxidised in an alkaline medium and the maximum current for this process is lower than in the oxidation of phenol by ~70%.[12] The substituent $C(CH_3)_3$ reduces somewhat the maximum substituted phenol oxidation current, the decrease of the current being observed in the following sequence as the position of the substituent is altered: *meta* > *ortho* > *para*.[2] It is believed[2] that, when the concentration of the corresponding phenol is 1×10^{-5} M, the current is limited by diffusion, which does not conflict with the experimentally observed independence of the current of the pH. However, a curve with a maximum, typical for diffusion currents at a stationary electrode, was not obtained.[2]

2. The Graphite Anode

Judging from the published data, all substituted phenols, which will be considered below, are oxidised at the anode and give rise to a single wave on the voltage–current curve. 2,6-t-Butylphenol and 6-t-butyl-2,4-dimethylphenol, which give rise to multiwave curves, are exceptions. The appearance of a maximum on the anodic curves for substituted phenols has been related[22] to $E_{1/2}$: if this potential is less than 0.48 V, a maximum may appear. The character of the current was not considered in the above investigation. However, it follows from the analysis of the literature data that a maximum is observed[23,26,27] on the potentiodynamic curves for the oxidation of many substituted phenols having $E_{1/2} < 0.48$ V (relative to the s.c.e.) at a pH other than in the study discussed above.[22]

The influence of substituents in the *m*-, *o*-, and *p*-positions on the oxidation current of phenols on the graphite anode in an aqueous medium has been examined in a number of studies[20,21,23,26,27,41] and it has been shown that resorcinol, catechol, and hydroquinone are readily oxidised over a wide pH range (1–9). At a catechol concentration of 1×10^{-3} M, a distinct limiting current is observed on the potentiodynamic curve but, with increase of concentration to 1.5×10^{-3} M, a maximum appears.[41]

The data concerning the appearance of a maximum on the voltage–current relations for resorcinol and hydroquinone are contradictory. Results showing the presence of a distinct limiting resorcinol oxidation current at a resorcinol concentration of 1×10^{-4} M [21] and the appearance of a maximum at a concentration of 4×10^{-4} M [26] are available. On the other hand, the presence of a distinct limiting current at a resorcinol concentration of 1×10^{-3} M has been reported.[41] Similar contradictions exist also for hydroquinone. Under identical conditions, and at equal hydroquinone concentrations [$(1.5–0.3) \times 10^{-3}$ M] a maximum has been observed in some studies[20,27,41], while in another[26] it was absent either owing to poor adsorbability or the dissolution of the oxidation product.

Table 2 shows the maximum oxidation current densities for substituted phenols and the initial phenol indicated in different sources differ appreciably from one another.

In the pH range 4–8 the maximum hydroquinone oxidation current hardly changes. The dependence of the resorcinol oxidation current on the pH has been investigated in only one study[22] and for this reason it is impossible to compare these data with other results.

In a number of investigations[20,21,23] the authors assumed without proof that the oxidation currents of aromatic dihydrocompounds ($c \leq 2.5 \times 10^{-4}$ M) are diffusional in nature. The fact that an increase of the rate of polymerisation increases the maximum current[20] cannot be regarded as unambiguous proof of the diffusional nature of the current, since this can be associated with a decrease of the adsorption of the reaction product. The oxidation currents of catechol and resorcinol in a weakly acid medium are higher approximately by a factor of 2 than the corresponding phenol current.[21] Hence, it was concluded that their oxidation requires twice as many electrons as the oxidation of phenol. However, when the solution is made alkaline up to pH 8.5, the maximum phenol, hydroquinone, resorcinol, and catechol oxidation currents become virtually identical (to within ±3%),[23] which may indicate the same process mechanism.

Table 2. The influence of the hydroxy-group on the maximum density of the oxidation currents of phenols (pH 5.0).

Compound	$10^3 i_{max}$, A cm^{-2}mol^{-1}	Conditions	v, mV s^{-1}	Refs.
Phenol	65	st.*	—	[20]
»	114	dyn.**	1.24	[21]
Hydroquinone	89	st.	—	[20]
»	114	dyn.	1.24	[21]
»	75	st.	8.3	[27]
»	81	st.	3.3	[30]
Resorcinol	207	dyn.	1.24	[21]
»	100	st.	8.3	[27]
»	64	st.	3.3	[30]
Catechol	168	dyn.	1.24	[21]
»	79	st.	8.3	[27]
»	58	st.	3.3	[30]

*Stationary conditions.

**Dynamic conditions.

An approximate calculation of the number of electrons participating in the primary hydroquinone oxidation electrode process has been carried out[20] from the corresponding potentiodynamic curves from the formula $E_{3/4} - E_{1/2} = 0.55n$. It has been noted that the rate of application of the potential influences n; for example, an increase of v by a factor of 2 induces a decrease of n by unity.

The behaviour of trihydroxybenzenes will be examined in relation to pyrogallol. At a concentration of this compound of 2.5×10^{-4} M in a neutral medium, an oxidation wave with a distinct maximum is observed: the maximum current is lower by ~30% than in the case of phenol.[23]

Several studies have been devoted to the influence exerted by the introduction of one methyl group in the *o*-, *m*-, and *p*-positions in the benzene ring of phenol on the oxidation current.[21-23,26] In aqueous buffer solutions at concentrations of cresols of 2.5×10^{-4} M and at pH from 4 to 11, an oxidation wave with a maximum has been observed. Table 3 presents the maximum oxidation currents for the above compounds. Evidently the data from different sources differ markedly.

A fairly complete idea about the dependence of the maximum oxidation currents of *o*- and *p*-cresols on pH can be obtained from Fig.6 (curves *1* and *2*).[26]

The dimethyl derivatives, namely 2,4-, 2,6-, and 3,4-dimethylphenols, are readily oxidised and distinct anodic waves with maxima are observed.[22,26] The introduction of two methyl groups diminishes the maximum oxidation current compared with phenol on average by 20–30%.[22,26] 3,5-Dimethylphenol, whose oxidation wave has no maximum and the height of the wave does not greatly exceed (by ~5%) the phenol oxidation current, is an exception.[26] The dependence of the maximum oxidation current for 2,6-dimethylphenol on the pH is illustrated in Figure 6 (curve *3*).[26]

Table 3. The influence of the position of the CH_3 substituent on the maximum density of the oxidation currents of phenols (pH 5.6).

Compound	Conditions*	$10^6 i_{max}$, A cm^{-2}	Refs.	Compound	Conditions*	$10^6 i_{max}$, A cm^{-2}	Refs.
Phenol	st.	19.0	[21]	*o*-Cresol	st.	10.7	[22]
»	st.	11.6	[22]	»	st.	38.0	[23]
»	st.	45.8	[23]	»	dyn.	16.0	[26]
»	dyn.	14.0	[26]	*p*-Cresol	st.	9.8	[21]
m-Cresol	st.	13.6	[22]	»	st.	9.6	[22]
»	st.	37.0	[23]	»	st.	32.4	[23]
o-Cresol	st.	14.0	[21]	»	dyn.	9.0	[26]

*For the significance of the abbreviations, see the references to Table 2.

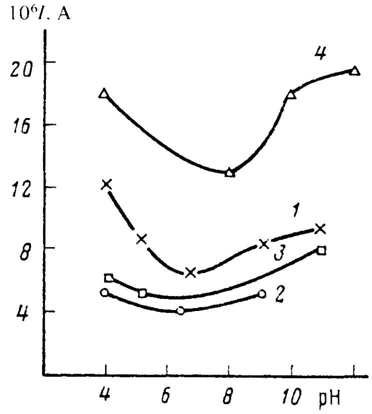


Figure 6. Dependence of the maximum oxidation currents for 4×10^{-4} M solutions of *o*-cresol (curve *1*), *p*-cresol (curve *2*), 2,6-dimethylphenol (curve *3*), and 2,4,6-trimethylphenol (curve *4*) on the pH.[26]

The behaviour of phenol after the introduction of three methyl groups into the benzene ring has been investigated in relation to 2,4,6-trimethylphenol. The absence of a maximum on its oxidation wave in phosphate (pH 7.0), acetate (pH 4.6), and aqueous alcoholic buffer solutions have been noted. The 2,4,6-trimethylphenol oxidation current in the pH range 4–12 exceeds by a factor of almost 2 the maximum phenol oxidation current (Fig.6, curve *4*).[26]

The introduction of one nitro-group into the benzene ring of phenol reduces the maximum phenol oxidation current at pH 8.5.[23,26] However, the data for the extent of this decrease are extremely contradictory. According to some data,[27] the decrease is on average ~90% at pH 8.5, while according to others[23] it is only ~13%. Similar differences in data persist also at other pH values. For example, it has been stated[22] that the maximum *p*-nitrophenol oxidation current at pH 5.6 is greater than that of phenol, while in another study[26] the opposite relation was observed at the same pH.

The oxidation of *m*- and *o*-aminophenols has been observed to generate a one-electron wave with a maximum, while the oxidation of *p*-aminophenol gives rise to a two-electron wave with a maximum.[23,27,31] The introduction of the amino-group into the *m*-position increases the oxidation current on average by 6%, while the *ortho*-substituent reduces the oxidation current by ~19%.[23]

The question of the mechanism of the electrochemical oxidation of aminophenol has been examined.[31] The character of the dependence of $E_{1/2}$ on pH and the analysis of the maximum current and the parameters $E_{1/2}/\Delta pH$ and $\Delta E/\Delta\,.\,\lg\,[i/(i_{\mathrm{lim}}-i)]$ justified the hypothesis that the observed oxidation waves on the graphite anode characterise the oxidation of the phenolic OH group, while the NH_2 group plays the role of an electrochemically inert substituent.

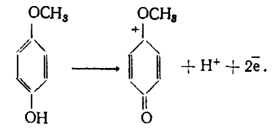
According to the data of Vodzinskii and Semchikova,[23] there is an oxidation wave with a maximum (pH 5.6) on the potentiodynamic curves for the oxidation of monochlorophenol, while other data[22] indicate waves without a maximum (pH 8.5). The difference is probably associated with the difference in the pH of the solution. At pH 5.6 the maximum oxidation currents of *p*- and *o*-chlorophenols are smaller than that of the initial phenol approximately by 15 and 13% respectively, while for *m*-chlorophenol it is greater by ~4%.[22] At pH 8.5 the *p*-chlorophenol oxidation current is lower by ~2% than that of phenol.[23]

A single oxidation wave without a maximum is observed on the potentiodynamic curve for the oxidation of 2,5-dichlorophenol at pH 5.6 and a concentration of 2.5×10^{-4} M, while the maximum oxidation current is lower by approximately 30% compared with phenol.[22]

The maximum oxidation currents for *p*- and *o*-phenylphenols oscillate markedly as the pH is altered: in borate buffer solution (pH 8.5), the current is higher by 6–8%, while in a weakly acid medium (pH 5.6) it is lower by 30–34% than for unsubstituted phenol.[22] The introduction of two phenyl substituents in the 2- and 4-positions lowers the maximum phenol oxidation current by ~31% (pH 5.6).[22]

Phenol with the COOH group in the *o*-position (salicylic acid) has a maximum oxidation current in an alkaline medium (pH 8.5), which is lower by ~31% than that of unsubstituted phenol, while in a weakly acid medium their maximum currents are virtually identical.[22,23] At pH 5.6 *o*- and *p*-ethylphenols have maximum oxidation currents lower by 20–24% than that of unsubstituted phenol, while the maximum oxidation current of *m*-ethylphenol is lower by only ~1.2%.[20,22]

All the monosubstituted methoxyphenols have oxidation currents in a weakly acid medium higher by 8% on average than the maximum oxidation current of the initial phenol.[22] The electrochemical behaviour of *o*-methoxyphenol has been investigated in an acid medium (0.1 M $HClO_4$ solution).[42] Two successive pairs of waves corresponding to the oxidation intermediates 3,3′-dimethoxydiphenoquinone and 3,3′-dimethoxy-4,4′-biphenol, *o*-quinone, and catechol have been observed on the cyclic voltage–current plot. The voltage–current plot for *p*-methoxyphenol (1.13×10^{-3} M) in 2.037 M H_2SO_4 solution shows an oxidation wave with a maximum, which corresponds to a two-electron process:[43]



The introduction of two OCH_3 groups in the 2- and 6-positions in the benzene ring leads to a decrease (at pH 5.6) of the maximum current (by 27%). If the OCH_3 group is introduced in the 2-position in *p*-cresol, the oxidation current increases by ~10%.[22] The influence of the ethoxy-substituents on the oxidation currents of the corresponding phenols was also investigated in the above study;[22] it was found that the *o*-substituent increases the maximum oxidation current of the substituted phenol by ~7%, while the *p*- and *m*-substituents respectively reduce the current by ~2% (this is within the limits of the accuracy of the measurement) and ~19%.

A distinct anodic wave has been observed in the electrochemical oxidation of *p*- and *o*-t-butylphenols in the pH range 5.6–8.5 at a low concentration (~10^{-4} M). The rates of oxidation of these compounds are lower than that of phenol by ~35 and ~55% respectively.[22,23]

The introduction of two and more $C(CH_3)_3$ groups into phenol leads to the appearance on the voltage–current curve of a maximum in aqueous buffer solutions, an example of such behaviour being provided by the oxidation of 2,6-di- and 2,4,6-tri-t-butylphenols.[23] The oxidation current falls in this case (by ~60%). However, it has been reported that 2,4,6-tri-t-butylphenol gives rise to an anodic curve with a distinct limiting current, which is independent of the pH,[44] in conflict with the data of Vodzinskii and Semchikova.[23]

The oxidation of 2,4,6-tri-t-butylphenol at a concentration of 1.11×10^{-3} M in an aqueous ethanol solution (at pH ranging from 0 to 10) at a vitreous carbon anode has been investigated by the cyclic voltamperometric method.[45] A wave with a maximum was observed in an acid medium, while in an alkaline medium two waves with maxima were noted.

After the additional introduction of the t-butyl group into the benzene ring of *o*- and *p*-cresols, the maximum oxidation current in aqueous buffer solutions falls by a factor of ~2.[22]

The appearance of three waves at once without maxima in the oxidation of 6-t-butyl-2,4-dimethylphenol at a concentration of 1×10^{-3} M in an aqueous buffer solution at pH 5.6 has been reported.[20] When the supporting electrolyte is acidified (to pH 1.2), the second wave disappears, while an increase in the alkalinity of the solution (to pH 10) leads to the disappearance also of the third wave. Following an increase of the rate of application of the potential by a factor of 2 (from 0.62 to 1.24 mV s^{-1}), the limiting oxidation current at pH 10 increases by 40–50%, as for unsubstituted phenol. When the temperature is raised by one degree in the range from 20° to 30 °C (at pH 5.6), the maximum currents on all three observed waves increase by 0.8, 2.7, and 5.2%. The temperature coefficients of the maximum currents on the first two waves correspond to the possibility of diffusional control of the oxidation process.

VII. PRACTICAL APPLICATIONS OF THE ELECTROCHEMICAL OXIDATION OF PHENOL AND ITS DERIVATIVES

As shown above, the anodic oxidation of phenol proceeds fairly readily. An important practical application of this process in the purification of phenol-containing waste water arose in this connection. In the solution of this problem, the advantages of the electrochemical method such as efficiency, reliability, low cost, and also the compactness of the electrolysers and the ease of automating the process have been noted.[47,48] Preliminary calculations have shown that, in the successful solution of this problem, the cost of the removal of phenol from 1 m^3 of water by electrochemical oxidation is lower by a factor of ~2 than the cost of the purification of water by ozonization and by a factor of ~5 than the cost of purification by adsorption on activated charcoal.[49] The above advantages of the electrochemical method have attracted the attention of many investigators, as shown by the numerous publications in this field.

The main bulk of studies have been carried out with graphite anodes. According to a review,[50] most of the studies on the electrochemical purification of waste water containing phenol have been devoted to the study of the oxidation of phenol in solutions containing chloride ions. The optimum oxidation conditions are as follows: alkaline medium (pH 9–11), $i = (4\text{–}8) \times 10^{-2}$ A cm^{-2}, and $c_{Cl} \cong 10\%$ for an initial phenol content in the waste water not exceeding 0.5 g $litre^{-1}$. The consumption of electrical energy on the oxidation of 1 g phenol using the electrochemically generated hypochlorite of the corresponding metal is 0.03–0.09 kWh.

The design of the electrolyser is important for the effective electrochemical oxidation of phenol. Electrolysers of the box or filter press types without a diaphragm are normally employed. The latter are preferable, since they make it possible to increase the electrode surface area to the maximum extent in a given volume by reducing the interelectrode gap and the dead space.

A report has been published[51] on the purification of factory waste water containing 2.5 g $litre^{-1}$ of phenol, 201 g $litre^{-1}$ of sodium chloride, and 4.6 g $litre^{-1}$ of sodium hydroxide on apparatus consisting of six BGK-12 baths connected in series. However, according to Sakharnov,[49] the purification was not carried out under optimum conditions.

There are also data indicating the employment of electrolysers with a powdered anode, made up of carbon-graphite materials, for the electrochemical purification of phenol-containing water.[52] The waste water was passed through the pre-polarised powdered anode, which made it possible to prevent the blocking of the pores by phenol and the oxidation products.

Industrial waste water contains as a rule several compounds of organic and inorganic origin; for this reason, an individual approach to the purification of each waste is necessary. Furthermore, the purification conditions developed on artificial solutions are not always suitable for the purification of real waste water. A comparison has been made[53] of the rates of oxidation of phenol in an artificially prepared solution and in industrial tar water. It was shown that the rate of oxidation of phenol in the tar water is close to the rate of its oxidation in the artificial solution, but, when identical amounts of chloride ions are added to the two solutions, the rate of oxidation of phenol in the industrial water increases more slowly than in the artificial solution.

We shall consider examples of the purification of industrial phenol containing waste water in electrolysers with insoluble anodes. In a study[54] of the electrolysis of the waste from the chemical coke industry, the simultaneous removal of oil (to the extent of 96%) by electroflotation and of phenol (to the extent of 30–40%) and cyanides (to the extent of 100%) by electrochemical oxidation was observed. The water was treated on a laboratory electrolyser with a horizontal cathode under which vertically arranged graphite anodes were placed. The electrolyser operating conditions were as follows: $i = 0.01$ A cm^{-2}, $\tau = 40$ min, and $t = 60\text{–}70$ °C. According to preliminary calculations, the cost of the purification of 1 m^3 of the waste water was 10–12 kopecks.[54] The low degree of removal of phenol from water, probably as a result of constructional deficiencies of the electrolyser, is noteworthy.

In the waste water from the Kherson petroleum processing works, it has been possible to reduce simultaneously by electrolysis the concentration of petroleum hydrocarbons from 0.29 to 0.016 g $litre^{-1}$, of phenols from 2×10^{-3} to 6.5×10^{-4} g $litre^{-1}$, of surfactants from 1.8×10^{-2} to 6.1×10^{-3} g $litre^{-1}$, and of inorganic substances from 5.5 to 3.8 g $litre^{-1}$.[55] The experiments were performed in a laboratory electrolyser with a vertical graphite anode and a zinc cathode under static conditions: $i = 8.5 \times 10^{-2}$ A cm^{-2}, $\tau = 40$ min, and $t = 40$ °C. The salt composition of the purified waste in the area of the anode and its design were not indicated in the relevant study,[55] but, judging from the figure quoted, the anode consisted of a rod placed in a spherical flask at a comparatively large distance from the analogous rod cathode. In our view, such design of the electrolyser is unsuitable for the practical electrochemical purification of waste water.

The purification of tar waters in an electrolyser with a cylindrical graphite anode has been reported;[53] at $i = 0.2$ A cm^{-2}, $c_{Cl} = 40$ g $litre^{-1}$, and $t = 60$ °C, the phenol concentration was reduced from 5.2 to 0.75 g $litre^{-1}$, i.e. by 85%, after the operation of the electrolyser for 1 h. However, at such high phenol concentrations it is more useful to employ the regenerative purification procedures.

The electrochemical oxidation of phenols, cyanide, and thiocyanates in the waste water from the enrichment works of the Zyryanovsk Lead–Zinc Combine has been investigated.[56] The experiments were performed in an electrolytic bath without a diaphragm containing graphitised carbon anodes. Before electrolysis, sodium chloride was introduced into the water to be purified; the purification was carried out at $i = 0.35 \times 10^{-2}\text{–}0.80 \times 10^{-2}$ A cm^{-2} and 20 °C. The waste water investigated[56] was characterised by a very low initial concentration of phenols, which diminished by only about 30% during the purification process.

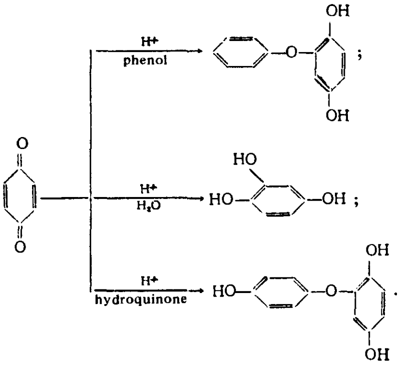
It has been suggested[53] that waste water containing phenols, thiosulphates, thiocyanates, and chlorides be purified by being passed downwards from above through a vertical cylindrical electrolyser with a platinum plate anode and an iron grid cathode. The electrolysis was carried out at $i = 0.8\text{–}0.12$ A cm^{-2} and the duration of the treatment ranged from 5 to 8 h. Under these conditions, the biological consumption of oxygen (BCO) in the waste water was reduced by 95%. However, the necessity to employ platinum as the anode material makes the process significantly more expensive.

The detoxication of the waste water from the coke chemical works by electrolysis at $i = 0.7\text{–}1.0$ A cm^{-2} has been investigated;[56] after electrical treatment for 5 h, the phenol concentration fell from 1.25 g $litre^{-1}$ (1.3×10^{-2} M) to 0.07 g $litre^{-1}$ (7.4×10^{-4} M). The consumption of electrical energy was 165 kWh m^{-3}. It is noteworthy that the process was performed at pH < 7.0, i.e. the conditions were not optimal for the oxidation of phenol by a hypochlorite.

An electrochemical method for the degradation of phenol by electrolysis at anodes with an active magnetite coating has been described.[57] Waste water containing 0.5 g $litre^{-1}$ of phenol and exhibiting a chemical consumption of oxygen (CCO) of 0.229 g $litre^{-1}$ was electrolysed at pH 7 and $i = 1.5 \times 10^{-2}\text{–}3.0 \times 10^{-2}$ A cm^{-2}. After electrical treatment for 2–5 min, the degree of elimination of phenols reached 95% and that with respect to the CCO was 77.8%; the consumption of electrical energy was 37 kWh m^{-3}. It is noteworthy that the use of the magnetite anode is technologically disadvantageous—it is brittle and has a relatively high electrical resistance.

In view of the requirement for large amounts of hydroquinone and alkylhydroquinones, especially in the photo- and cine-industry, the method of their synthesis by oxidising the corresponding phenols is of great practical interest. Such attempts have already been made for a long time,[58–62] but the required substance was obtained in a low yield and was impure. The oxidation process and the composition of the reaction products depend to a large extent on the phenol concentration, the electrolyte temperature, the pH of the solution, and other parameters. Depending on the electrolysis conditions, many compounds are formed, some of which may prove useful.

Under ideal conditions, quinone is formed on the anode and, after reduction at the cathode, is fully converted into hydroquinone. In reality ring-opening products (oxalic and maleic acids) as well as compounds obtained as a result of the total degradation of phenol (carbon dioxide and monoxide) are formed together with the required substance. Tarry substances are also formed in a considerable amount, apparently as a result of secondary reactions,[63,64] which may involve the interaction of *p*-benzoquinone with phenol. In the presence of hydrogen ions, this leads to the formation of phenoxyhydroquinone; under analogous conditions, the interaction of *p*-benzoquinone with hydroquinone affords hydroxyphenoxyhydroquinone. The interaction of *p*-benzoquinone with water in an acid medium leads to the formation of hydroxyhydroquinone:



The above side reactions not only reduce the current and material yield of phenol but also hinder the isolation and purification of the required substance.

An appreciable reduction of the amount of side products formed can be achieved by carrying out the electrolysis of aqueous sulphuric acid solutions (acid concentration 1 to 5 wt.%) in a diaphragm electrolyser with added phenol at a concentration of 0.5–4.0 wt.%.[64,65] During electrolysis, the pH was maintained at <4.0, the anodic potential was 0.9 V (relative to the s.c.e.), the cathodic potential was <–0.4 V, $i = 0.2–0.4$ A cm^{-2}, and $t = 50–60$ °C. Under these conditions, the material yield of hydroquinone was ~50% and the current yield was ~85%.[64] An apparatus which makes it possible to isolate fairly pure *p*-benzoquinone from the reaction mixture has also been described in detail. If conditions optimal for the preparation of *p*-benzoquinone are used, the material yield of alkylquinones is only 20%.

It has been shown[66] that, in acetonitrile solutions, dimethylphenol is oxidised to dimethylquinone. However, the attempts to reduce this substance to the corresponding hydroquinone were unsuccessful. Alkylhydroquinones having the general formula $C_6H_{(6-x)}R_xO_2$ (where R is an alkyl group containing up to four carbon atoms and x ranges from 1 to 3) can be obtained in satisfactory yields by oxidising the corresponding phenols.[66]

The electrochemical oxidation of 2-methyl-, 2,6-dimethyl-, 2,3,6-trimethyl-, and 2,3,5-trimethyl-phenols has been carried out[66] in an electrolyser with a cation-exchange diaphragm. The anode was made from lead dioxide and the anolyte employed consisted of a 1:1 water–acetone mixture containing 0.5 M sulphuric acid; the cathode was made of lead, the catholyte consisted of a 0.5 M aqueous sulphuric acid solution, and $i = 0.12–0.15$ A cm^{-2}. Under these conditions, the material yield of 2,6-dimethyl-*p*-benzoquinone was 86% and the current yield was 55%. At the end of the reaction, the anolyte was transferred to the cathodic compartment and the quinone was reduced to hydroquinone; the yield of 2,6-dimethylhydroquinone (purity 90%) with respect to the phenol which had reacted was 65%. Other alkylhydroquinones were obtained in similar yields.[66] Thus the process leads to the possibility of obtaining hydroquinone also from waste water containing phenol at a fairly high concentration.

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Thus the kinetics of electrode processes in the electrochemical oxidation of phenol have been investigated in detail on the basis of extensive experimental data on this subject. It has been shown that phenol-containing waste water can be purified electrochemically and alkylhydroquinones can be obtained; however, some of the problems arising in the practical application of this procedure have not as yet been satisfactorily solved.

In the first place, in the majority of applied studies there has been no scientifically based approach to the selection of optimum process conditions, in particular the current density; for this reason, as regards experimental data, many parameters are selected at random. There is a clear gap between theoretical studies on the kinetics of the oxidation of phenol and practical electrolysis. There is insufficient information about the adsorption of phenol on platinum and graphite anodes and contradictory data have been obtained for the influence of chloride ions on the rate of oxidation of phenol. The cause of the inhibition of the oxidation of phenol observed in kinetic studies has not yet been established. If this could be done, the problem of the activation of the electrode under continuous conditions could be solved.

In the study of the waste water purification processes, little attention has been devoted to the analysis of the electrolysis products; the necessary conditions guaranteeing the complete oxidation of phenol to carbon dioxide and water have not been established. Relatively unproductive and difficult to service electrolysers of the box type are as a rule recommended for the purification of waste water. The question of the application of highly effective electrolysers with bulk electrodes in the purification process has so far been little studied.

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The Reactions of Hydrocarbons under the Influence of Transition Metal Atoms and Ions in the Gas Phase at Room Temperature

B.A.Dolgoplosk, I.A.Oreshkin, and T.V.Soboleva

The results of numerous experimental studies of the composition of the products fromed on interaction of hydrocarbons with transition metal atoms or ions in the gas phase at room temperature are surveyed. In all cases organometallic intermediates are formed, their decomposition leading to the final reaction products. The results presented are of great interest for the understanding of the chemical nature of the elementary steps in the reactions of hydrocarbons in heterogeneous catalysis. The bibliography includes 68 references.

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I. INTRODUCTION

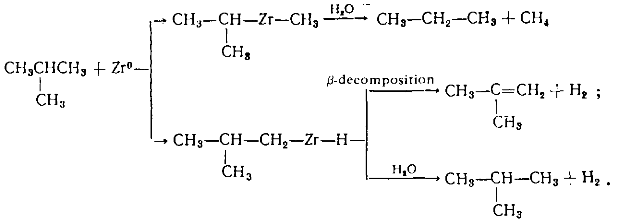
The modern ideas about the mechanisms of the elementary steps in the reactions of hydrocarbons under the influence of transition metals in heterogeneous catalysis presuppose the preliminary dissociative adsorption of the hydrocarbons on the catalyst surface with formation of radical-like fragments, which consist of hydrocarbon groups or hydrogen atoms, and are in some way linked to the heteroatoms, and are capable of migrating from one active centre of another. As a rule catalytic reactions proceed with participation of a large number of active centres; this applies particularly to the hydrogenolysis and skeletal isomerisation reactions of hydrocarbons under the influence of transition metals. In view of the lack of direct experimental approaches to the study of the chemistry of the elementary steps in heterogeneous catalysis, the idea that different active centres and intermediate hydrocarbon species, whose chemical nature is obscure, participate in different reaction stages is frequently resorted to. In earlier publications, we examined the chemistry of the elementary steps in hydrogenation, dehydrogenation, hydrogenolysis, and deuterium exchange processes on the basis of the idea that the primary reaction involves the oxidative addition of hydrocarbons to a transition metal atom on the surface with subsequent decomposition of the resulting organometallic compound.[1-3] Thus it has been suggested that hydrogenation in heterogeneous systems proceeds via stages in which the olefin adds to the H–N hydride bond and that a hydrogen molecule adds to the C–M bond with regeneration of the initial hydride derivative, while the dehydrogenation reaction includes a stage in which the hydrocarbon undergoes oxidative addition to the reduced metal with subsequent β-decomposition of the organometallic intermediate. This made it possible to explain the primary formation of but-1-ene observed in the heterogeneous catalytic dehydrogenation of butane. The specific deuterium-exchange reactions involving various hydrocarbons in the initial stages and the mechanism of the autohydrogenation of unsaturated hydrocarbons have also been examined on the basis of these ideas. The pathways leading to the decomposition of organometallic compounds of transition metals frequently used in heterogeneous catalysis (Ni, Co, Pt, Pd, W, Mo, Rh, Cr, etc.) have been recently studied in detail in relation to various alkyl and aryl derivatives. They decompose mainly via β-elimination, which leads to the formation of equimolar amounts of alkenes and alkanes, and α-decomposition accompanied by the formation of extremely reactive carbene and carbyne species and recombination products produced from the hydrocarbon groups linked to the metal. The chain metathetical reactions of olefinic hydrocarbons under the influence of W, Mo, Re, and Ta compounds are known to be initiated by the carbene complexes formed on α-decomposition of organometallic compounds. The mechanisms of all these reactions have been described in detail in a series of reviews.[4-8] Naturally, the metal atoms which retain the greatest number of free coordination sites and whose reactivity approaches that of isolated atoms are the most reactive in the oxidative addition reactions of hydrocarbons. The metal atoms on the crystal faces, in dislocations, and, as will be shown below, in the gas phase and in the hydrocarbon matrix may play a similar role.

Not only zerovalent metals but also metals in low oxidation states are sometimes fairly active in similar reactions, as shown for the addition of toluene to biscyclopentadienyltungsten[9] and of triphenylphosphine to a series of Group VIII metals.[10] The contribution of the homolytic decomposition of the organometallic compounds, accompanied by the formation of free radicals is small and thus should apparently increase with increase of reaction temperature. However, a high selectivity of the action of catalysts at elevated temperature is incompatible with the occurrence of free-radical stages in the process, which indicates the need to take account of other pathways which have been investigated for the reactions of organometallic intermediates.

Numerous publications devoted to the study of the reactions of hydrocarbons with metal atoms in hydrocarbon matrices at reduced temperatures or with metal ions in the gas phase at room temperature have appeared recently. The composition of the products of these reactions shows that the latter take place via stages in which the metal adds to the C–H or C–C bond with subsequent reaction of the organometallic intermediate. These investigations are of great interest for the understanding of the chemical nature of the elementary steps in heterogeneous-catalytic reactions of hydrocarbons and can serve as an experimental basis for the examination of the reaction mechanisms. This review presents a survey of the results of the published studies in this field.

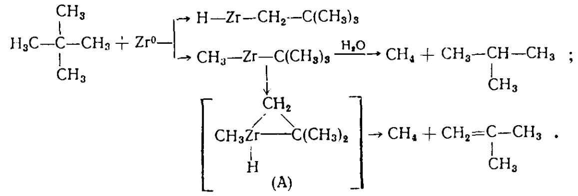
II. THE REACTIONS OF HYDROCARBONS WITH METAL ATOMS

The possibility of the chemical interaction of metal atoms with alkanes was established for the first time in 1979.[11] The authors showed that the reaction of zirconium atoms, obtained by evaporation in a high vacuum, with isobutane or neopentane in a matrix begins already at -196 °C. Heating of the hydrocarbon matrix to room temperature is accompanied by the evolution of a certain amount of hydrogen and of traces of methane. Subsequent hydrolysis of the matrix leads to the formation of considerable amounts of hydrogen and C_1–C_4 hydrocarbons in the case of isobutane and C_1–C_5 hydrocarbons in the case of neopentane. The main products of the first reaction were isobutene and methane and those of the second were methane, isobutane, and isobutene. The results enabled the authors to conclude that the zirconium undergoes oxidative addition to the C–H or C–C bonds of isobutane and neopentane with subsequent decomposition of the organometallic compounds formed:



(1)

The following reaction mechanism has been proposed for neopentane:



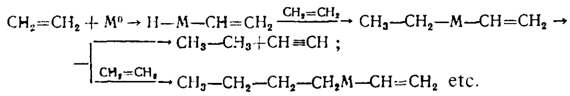
(2)

The presence of isobutane in the products of the reaction of zerovalent zirconium with neopentane is apparently associated with the hydrolysis of the organometallic compounds formed as a result of the insertion of the metal in the C–C bond. Although the hypothesis of the formation of the intermediate state (A) is controversial, it is difficult to imagine other pathways leading to the formation of isobutene and methane—products which are characteristic of the reaction of neopentane under the conditions of heterogeneous catalysis at high temperatures.

It has been shown[11] that many other transition metals (Ti, V, Cr, Mn, Fe, Ni, Co, Mo, and W) can undergo oxidative addition to isobutane under the same conditions with formation of the decomposition products of the organometallic intermediates.

The decomposition products of organometallic intermediates have been detected in studies[12,13] of the condensation of zerovalent nickel vapour on pentane, 2,3-dimethylbutane, methylcyclopentane, and cyclopentane at -196 °C.

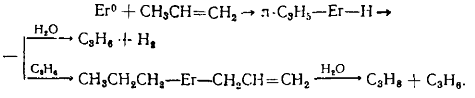
The interaction of the vapours of metallic ytterbium, samarium, and erbium, with ethylene, propene, and allene and also the reaction of erbium with cyclopropane at -196 °C have been investigated.[14] Organolanthanide compounds stable at room temperature were obtained. The product of the reaction of erbium with propene, apparently a π-allyl complex, proved to be soluble in tetrahydrofuran (THF). A small amount of hydrogen was found among the products of the hydrolysis of the organometallic compounds obtained in all the systems. The composition of the main hydrolysis products depended on the nature of the metal and the hydrocarbon. Thus the hydrolysis of the ethylene matrix with ytterbium and samarium led to the formation of C_1–C_6 hydrocarbons, which indicates the oligomerisation of ethylene under the influence of organometallic lanthanide compounds. The main hydrolysis product in the erbium–ethylene system was methane (90%):



(3)

The methane formed is apparently the product of the hydrolysis of the carbide produced as a result of the interaction of the zerovalent metal with acetylene. An analogous explanation was put forward by ourselves[3] in a study of the mechanism of the autohydrogenation of olefins.

Propyne, propane, propene, and the initial allene were found among the principle hydrolysis products in the reaction involving allene or in this reaction the products were propane, propyne, and the initial propene. On the basis of the considerations concerning the role of the organometallic intermediates and their decomposition pathways put forward in our earlier studies,[1-3] the reactions of propene can be accounted for in terms of the mechanisms



(4)

The hydrolysis of the erbium–cyclopropane matrix led to the formation of mainly the propane–propene fraction, propyne, and the initial cyclopropane. The data obtained led to the conclusion that the reactions in the systems investigated have a complex mechanism and that oxidative addition of the metal to the C–H bond takes place in all cases.

The oxidative addition of lanthanides to the C–H bond has been observed for hydrocarbons containing weakly acidic hydrogen. Thus the interaction of ytterbium, samarium, and erbium with hex-1-yne at -196 °C leads to the formation of lanthanide hydride compounds.[15] The formation of neodymium hydride in the decomposition of its butyl derivatives, obtained by the exchange reaction of $(C_5H_5)_3Nd$ with n-BuLi, has been observed.[16]

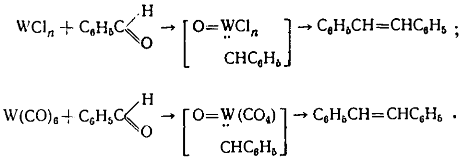
An infrared spectroscopic study of the photoinitiated reaction of copper atoms in a methane matrix at -261 °C demonstrated[17] the formation of organometallic compounds of the type CH_3MH. The formation of analogous compounds on photoinitiation had been observed earlier[18,19] in the reactions of iron, cobalt, copper, manganese, and lanthanide atoms with methane at -253 °C.

The infrared spectroscopic method made it possible to establish the insertion of a photoexcited iron atom in the C–H bond of ethane and propane at -263 °C.[20] The formation of a metallocyclobutane derivative, the product of the insertion in the C–C bond, was observed for cyclopropane.

The reaction of ethylene with cobalt, rhodium, nickel, and palladium atoms at -261 °C was investigated by infrared spectroscopy under conditions involving matrix isolation.[21] The formation of only the π-complex with ethylene was observed in all cases; this may be regarded as the primary reaction stage leading to the insertion of the metal in the C–H bond at higher temperature.

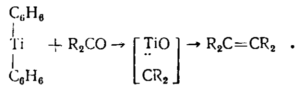
III. THE REACTIONS OF CARBONYL COMPOUNDS WITH METALS IN LOW OXIDATION STATES

Not only the atoms of transition metals but also their other forms corresponding to low oxidation states can enter into the oxidative addition reactions. This has been established for the interaction of aldehydes and ketones with tungsten and titanium compounds in which the metal is in a reduced state. Thus it has been shown that the addition of benzaldehyde to the WCl_6-2RLi system in THF at room temperature induces the rapid formation of stilbene.[22] According to the data of Fujiwara et al.,[23] the $WCl_6-LiAlH_4$ system is just as active in this reaction, while tungsten and molybdenum carbonyls have somewhat lower activities. The formation of olefins from carbonyl compounds in the electrochemical reduction of WCl_6 has been observed.[24] The formation of stilbene as a result of the oxidative addition of benzaldehyde to reduced metals can be represented schematically as follows:



(5)

Ledon et al.[25] investigated the reductive dimerisation of aldehydes and ketones under the influence of a zerovalent titanium complex–bisbenzenetitanium. The reactions of benzophenone and acetone with bisbenzene-titanium at 75–80 °C in THF led to the formation of tetraphenylethylene and tetramethylethylene respectively in quantitative yields. Presumably the reaction proceeds via the mechanism



$$\underset{C_6H_6}{\overset{C_6H_6}{\overset{|}{\underset{|}{Ti}}}} + R_2CO \rightarrow \left[\underset{CR_2}{\overset{}{\underset{\cdot\cdot}{TiO}}}\right] \rightarrow R_2C{=}CR_2 \ .$$

(6)

IV. OXIDATIVE ADDITION OF HYDROCARBONS TO TRANSITION METAL IONS

Numerous studies devoted to the gas-phase reactions of hydrocarbons at room temperature and in a high vacuum with the univalent ions of a whole series of transition metals (Rh^+, Fe^+, Co^+, Ni^+, Cr^+, and Sc^+) have been published recently. The reactions of alkanes,[26–36] alkenes,[31,37–40] cyclic hydrocarbons,[26,27,35,41,42] and their derivatives, namely alkyl halides,[43–47] alcohols,[44,45] aldehydes and ketones,[48–50] ethers,[48,49] amines[51,52] and nitro-compounds,[53] have been investigated. Transition metal ions have been obtained with the aid of laser radiation,[26–28,37,41,46] by thermal ionisation,[32–36, 40,42,50,53] or under the influence of the electron impact.[29–31,38, 39,43,45,47–49,51,52] The gas-phase reactions of the ions were investigated mass-spectrometrically. Naturally, the energy levels of the metal ions transferred to the gas phase differ significantly depending on the nature of the metal and the conditions of their formation which indicates influence on the character of the product formed, in particular on the relative contributions of the reactions involving insertion in the C–H and C–C bonds. In this connection, the high reactivity of the isolated metal atoms and ions in the gas phase means that their interaction with hydrocarbons at room temperature leads to the formation of the same products as in heterogeneous catalysis at high temperatures.

The composition of the primary products of the interaction of hydrocarbons with Rh^+, obtained by irradiating rhodium foil with a laser beam in the presence of the reacting hydrocarbon, has been investigated mass-spectrometrically.[26] The contribution by secondary reactions does not exceed 10%. The results of this study, presented in Table 1, are of significant interest for the understanding of the chemical nature of the elementary steps in the catalytic reactions of hydrocarbons under the influence of individual metal atoms or ions.

In the reactions of ethane and propane, olefins bound in complexes are formed quantitatively (or almost quantitatively), while the reactions of n-butane, n-pentane, and 2,3-dimethylbutane give rise to dienes with evolution of the corresponding amount of H_2. Trienes bound in complexes are formed from n-heptane and n-octane with evolution of three H_2 molecules.

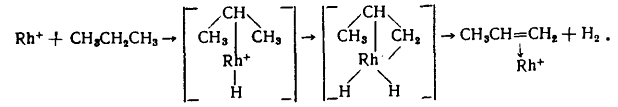
Table 1. The composition of the primary products of the reactions of Rh^+ with alkanes at room temperature.[26]

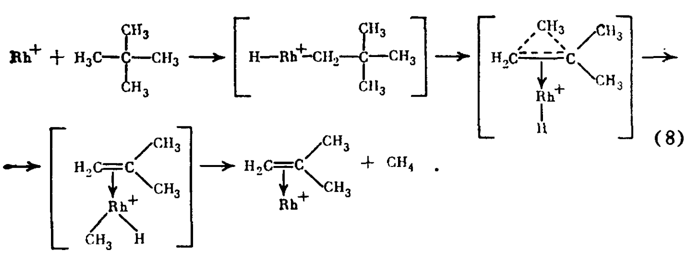
Alkane	(RhA)+	Yield $(RhA^+)^*$, %	Neutral products
C_2H_6	$RhC_2H_4^+$	100	H_2
C_3H_8	$RhC_3H_6^+$	94	H_2
n-C_4H_{10}	$RhC_4H_6^+$	100	$2H_2$
iso-C_4H_{10}	$RhC_4H_8^+$	43	H_2
	$RhC_4H_6^+$	48	$2H_2$
n-C_5H_{12}	$RhC_5H_8^+$	88	$2H_2$
iso-C_5H_{12}	$RhC_5H_8^+$	97	$2H_2$
neo-C_5H_{12}	$RhC_5H_{10}^+$	15	H_2
	$RhC_5H_8^+$	29	$2H_2$
	$RhC_4H_8^+$	13	CH_4
	$RhC_4H_6^+$	34	H_2, CH_4
n-C_6H_{14}	$RhC_6H_{10}^+$	49	$2H_2$
	$RhC_6H_8^+$	33	$3H_2$
	$RhC_6H_6^+$	18	$4H_2$
$CH_3-\underset{CH_3}{\underset{\vert}{CH}}-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$	$RhC_6H_{10}^+$	100	$2H_2$
n-C_7H_{16}	$RhC_7H_{10}^+$	94	$3H_2$
n-C_8H_{18}	$RhC_8H_{12}^+$	91	$3H_2$
Cyclopropane	$RhC_3H_4^+$	76	H_2
	$RhCH_2^+$	11	C_2H_4
Cyclopentane	$RhC_5H_6^+$	100	$2H_2$
Cyclohexane	$RhC_6H_8^+$	65	$2H_2$
	$RhC_6H_6^+$	35	$3H_2$

*Relative to theoretical yield.

The principle products of the reaction of n-hexane are complexes of a diene and triene as well as benzene, which is apparently formed from the linear triene via the intermediate cyclohexadiene. It has been shown[54,55] that the dehydrocyclisation of hexane to benzene in heterogeneous catalysis at high temperatures proceeds via consecutive stages involving the formation of an olefin, a diene, a triene, and cyclohexadiene. Complexes of isobutene and butadiene are formed in approximately equal amounts from isobutane. The formation of butadiene indicates the occurrence of skeletal isomerisation together with dehydrogenation. The neopentane reaction products are of special interest. Apart from the isopentene and isoprene complexes, arising as a result of consecutive steps involving the isomerisation of neopentane and its dehydrogenation, complexes of butene and butadiene with the metal, formed as a result of the decomposition of the hydrocarbon skeleton with the simultaneous evolution of CH_4 and H_2, were also detected. As expected, a complex of cyclopentadiene is formed in a quantitative yield from cyclopentane, while the complexes of cyclohexadiene and benzene are formed from cyclohexane. It is of interest to note that a complex of methylene carbene was formed in a yield of approximately 11% from cyclopropane. All these reactions are characteristic of heterogeneous catalysis by transition metals at high temperatures.

It has been concluded[26] that the primary step is the oxidative addition of the hydrocarbon with formation of the organometallic derivative and the decomposition of the latter leads to the final reaction products. Thus the following mechanisms have been proposed for propane and neopentane:

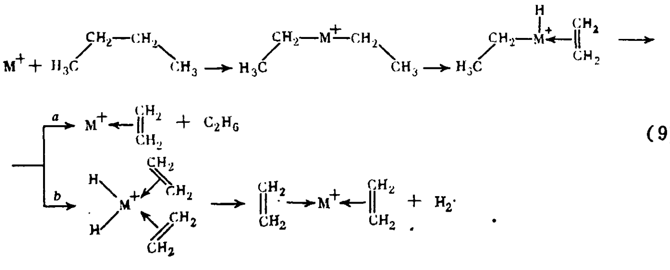

(7)


(8)

It is noteworthy that the insertion of the metal in a C–H bond in the methyl group, and not in the methylene group as in Eqn.(7), appears to us preferable, since this involves the formation of a more stable primary organometallic intermediate. The decomposition of the latter via the β-elimination pathway leads to the formation of the same reaction products.

The reactions of normal and branched alkanes as well as cycloalkanes with Ti^+ ions obtained by the action of laser radiation on titanium foil were investigated in a subsequent study.[27] The Ti^+ ions are inserted mainly in the C–H bonds of hydrocarbons, leading to the formation of products similar to those obtained in the presence of Rh^+ ions.

The reactions of Fe^+, Co^+, and Ni^+ ions with a series of normal alkanes ranging from propane to heptane have been investigated.[28] The Fe^+, Co^+, and Ni^+ ions were obtained by the same method as the Rh^+ and Ti^+ ions. It was found that the Ni^+ and Co^+ ions are mainly inserted in a C–C bond with formation of unsaturated products of the decomposition of the carbon skeleton:


(9)

If the metal is inserted in the $CH_2–CH_3$ bond in n-butane, then the same reaction leads to the formation of propene and methane. Diethylcobalt, obtained by the reaction of ethyllithium with $CoCl_2$, is known to decompose only via pathway (9a), leading to the formation of equimolar amounts of ethane and ethylene.[56] Such products can arise not only via each stage involving the formation of a hydride derivative, as in reaction (9a), but also as a result of the disproportionation of two ethyl groups bound to the metal. Reaction (9b), which leads only to ethylene, does not occur in this case. It may be that this reaction is specific to metal ions. In the case of Fe^+, the insertion in a C–H bond with subsequent formation of an olefin is observed together with the above reaction.

The study of the reactions of a series of olefins, ranging from ethylene to hexene isomers, in the presence of Fe^+ ions obtained with the aid of laser radiation has shown that the composition of the primary reaction products depends on the nature of the olefin.[37] Ethylene, propene, and isobutene did not react with Fe^+ ions under these conditions. n-Butenes give rise to quantitative yields of products of the insertion in a C–H bond. In contrast to n-butenes, methylbutenes produce considerable amounts of products of the insertion in a C–C bond. In the reactions of n-pentenes and hexenes, the last of the reactions indicated becomes the main one.

The reactions of Fe^+, Co^+, and Ni^+ ions with cyclic hydrocarbons, namely cycloalkanes and cycloalkenes, have also been investigated.[41] In this case the reaction involving the insertion of the metal ion in a C–C bond is the main one, which is the reason for the formation of products of the dehydrogenation and rupture of the carbon skeleton, as has been noted for the reactions of Co^+ and Ni^+ with n-alkanes.

It has been established that the presence of the hydride ligand[57] influences significantly the reactivity of the metal ions. This conclusion was reached on the basis of the study of the reactions of FeD^+, CoD^+, and NiD^+ with a series of alkanes ($C_1–C_5$) and alkenes (C_2 and C_3) in the gas phase. The FeD^+, CoD^+, and NiD^+ ions were generated by the reaction of the Fe^+, Co^+, and Ni^+ ions, obtained by laser radiation, with deuteriated nitromethane or methyl nitrite:

$$M^+ + CD_3NO_2 \xrightarrow[-NO]{} MOCD_3^+ \xrightarrow[-CD_2O]{} MD^+ ;$$
$$M^+ + CD_3ONO \xrightarrow[-NO]{} MOCD_3^+ \xrightarrow[-CD_2O]{} MD^+ . \qquad (10)$$

It was found that the FeD^+, CoD^+, and NiD^+ ions are inserted mainly in C–H bonds of the alkanes, in contrast to the Co^+ and Ni^+ ions, which, as shown above, give rise mainly to products of the insertion in a C–C bond. NiD^+ and CoD^+ are then capable of reacting with ethane, while NiD^+ is capable of oxidative addition even to methane.

It was noted above that the Fe^+ ion does not react with ethylene and propene. On the other hand, FeD^+ and CoD^+ can undergo oxidative addition to the C=C bond of propene and NiD^+ also to the C=C bond of ethylene.

According to the data of Jacobson and Freiser,[58] $CoCH_3^+$ as well as MH^+ ions are inserted solely in a C–H bond of aliphatic alkanes, starting with propane. This fact has been established in a study of gas-phase reactions of $CoCH_3^+$ with a series of alkanes ranging from methane to hexane isomers. The $CoCH_3^+$ ions were obtained by the reaction of Co^+, generated by laser radiation, with methyl iodide:

$$Co^+ + CH_3I \rightarrow CoCH_3^+ + I . \qquad (11)$$

The authors showed that methane and ethane do not react with $CoCH_3^+$. The evolution of mainly methane and the formation of dehydrogenation products were observed in the reactions with participation of $C_3–C_6$ alkanes. In the reactions of 2,2-dimethylpropane and 2,2-dimethylbutane, methane is the main neutral reaction product (insertion in a C–C bond).

The $FeCH_3^+$ ions, obtained by the same method as the $CoCH_3^+$ ions, do not react with aliphatic alkanes.[58] The reactions of the $NiCH_3^+$ ions have not been investigated, since they could not be obtained by the above method. The formation of NiI^+ and not $NiCH_3^+$ was observed in the reaction of Ni^+ with methyl iodide.

The gas-phase reactions of the $CoCH_3^+$ and $FeCH_3^+$ ions with a series of cyclic hydrocarbons—cycloalkanes ranging from C_3 to C_6 as well as cyclopentene and cyclohexane—were subsequently investigated.[59] These ions are inserted mainly in C–C bonds of cyclopropane and cyclobutane, forming alkyl (ethyl or propyl) complexes and ethylene. It had been shown earlier that the Fe^+ and Co^+ ions, obtained by means of laser radiation, do not react with cyclopropane.[41] In the reactions of cyclopentane, cyclohexane, cyclopentene and cyclohexene with $CoCH_3^+$, the formation of only the dehydrogenation products (the complexes of cycloalkenes or cycloalkadienes) and the corresponding neutral products (methane and hydrogen) was observed. The $FeCH_3^+$ ions do not enter into this reaction. In the case of cyclopentene and cyclohexene the oxidative addition to a C–H bond is the only reaction for both $CoCH_3^+$ and $FeCH_3^+$.

In one of the most recent studies,[60] the gas-phase reactions of the $FeCH_2^+$ and $CoCH_2^+$ ions with aliphatic alkanes are investigated. The method of preparation of the MCH_2^+ ions was based on the reactions of the Fe^+ and Co^+ ions, generated by laser radiation, with epoxyethane or cycloheptatriene:

$$M^+ + C_2H_4O \rightarrow MCH_2^+ + CH_2O$$
$$M^+ + \text{cyclo-}C_7H_8 \rightarrow MCH_2^+ + C_6H_6 \quad (12)$$

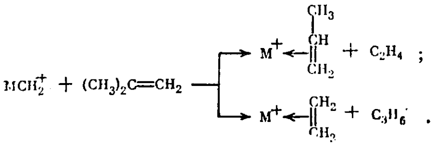
The study of the reactions of the $CoCH_2^+$ and $FeCH_2^+$ ions with alkanes, ranging from methane to hexane isomers, led to the conclusion that the oxidation addition of the hydrocarbon to the metal ion proceeds predominantly via the insertion into the C–H bonds of the alkanes and to a lesser extent the C–C bonds. The $CoCH_2^+$ ion reacted with all the alkanes investigated except methane, while the $FeCH_2^+$ ions reacted with alkanes starting from propane.

The gas-phase reactions of the $FeCH_2^+$ and $CoCH_2^+$ ions with olefins, ranging from ethylene to hexene, and also with butadiene, acetylene, and propyne have also been studied.[61] The reactions of $FeCH_2^+$ and $CoCH_2^+$ with ethylene lead to the formation of only the M^+ ion and the corresponding neutral product C_3H_6. The authors suggest that the interaction of $CoCH_2^+$ with ethylene may entail its insertion both in a C–H bond with formation of propene and in the C=C bond with formation of cyclopropane. The reaction of the $FeCH_2^+$ ion may result in the formation of propene alone. The study of the interaction of ethylene with MCD_2^+ ions established the occurrence of a metathetical reaction, which was inferred from the presence of the products MCH_2^+ and $C_2H_2D_2$. Thus two processes take place:

$$MCD_2^+ + CH_2{=}CH_2 \rightarrow MCH_2^+ + CD_2{=}CH_2\ ; \quad (13a)$$

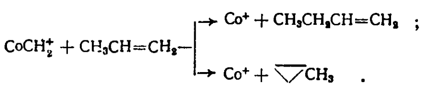
(13b)

In the case of ethylene the contribution by reaction (13a) is small, amounting to 20% for the $FeCH_2^+$ ions and only 2% for the $CoCH_2^+$ ions. However, the contribution of the metathetical reaction increases significantly in the case of propene and isobutene. Thus the main product of the reaction of MCH_2^+ with propene is the ion of ethylene bound in a complex, while isobutene gives rise mainly to the ions of ethylene and propene bound in complexes:



(14)

Apart from the ions indicated, the M^+ ions were found in the products of the reactions of MCH_2^+ with propene and isobutene, as well as the compounds C_4H_8 in the former case and C_5H_{10} in the latter. The authors[61] believe that the $CoCH_2^+$ ions can be inserted both in a C–H bond of propene to form but-1-ene, and in the C–C bond to form methylcyclopropane:



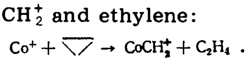
(15)

In the reaction of $FeCH_2^+$, only the insertion in a C–H bond is possible. In contrast to propene, isobutene gives rise to an appreciable amount of $MC_4H_6^+$ ions. n-Butenes give rise to the same main reaction product as isobutene. A complex set of products has been obtained in the reactions of pentenes and hex-1-ene. The main products of the reaction of the MCH_2^+ ions with butadiene were the M^+ ion and the corresponding neutral compound C_5H_8, which is cyclopentene according to the authors. In the case of acetylene and propyne, a single reaction leading to the formation of M^+ was observed in each case together with the products C_3H_4 (from acetylene) or C_4H_6 (from propyne). The authors[61] suggest that only the insertion of the carbene in a C–H bond with formation of an allene or propyne is possible in the first of the above reactions.

The reactions of alkanes with the Fe^+, Co^+, and Ni^+ ions[32–35] and of alkenes and cycloalkanes with Co^+[40,42] have been investigated by the method of ion beams. The ions were obtained by the thermal ionisation of metals formed on decomposition of the corresponding chlorides. The composition of the products of the reactions of alkanes ranging from butane to octane with the Fe^+, Co^+, and Ni^+ ions having a kinetic energy of approximately 0.5 eV permitted the same conclusion as that reached by Jacobson and Freiser,[28] namely that the Ni^+ and Co^+ ions are inserted preferentially in a C–C bond and that this is accompanied by insertion in a C–H bond in the case of Fe^+.

The study of the interaction of Co^+, having a kinetic energy of approximately 1 eV, with alkenes ranging from ethylene to hexenes[40] showed that ethylene and propene do not react with the metal ions under these conditions. In the case of isobutene the products of the insertion of Co^+ in a C–C bond was found. The reactions of n-butenes with Co^+ led to the formation of mainly a diene bound in a complex and of the corresponding neutral product (H_2). In the reactions of pentenes and hexenes, the insertion in both C–H and C–C bonds was observed.

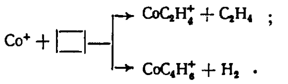
The results obtained in a study[42] of the gas-phase reactions of Co^+ ions, having a kinetic energy of approximately 1 eV, with cycloalkanes ranging from cyclopropane to cyclohexane diverge somewhat from the data of Jacobson and Freiser.[41] Under these conditions, the Co^+ ions react with cyclopropane with formation of $CoCH_2^+$ and ethylene:



(16)

The absence of the reactions of cyclopropane with Fe^+, Co^+, and Ni^+, generated by the influence of laser radiation, is apparently associated with the fact that these ions exist mainly in the ground and insufficiently excited electronic states and do not have a high kinetic energy compared with the ions used in the ion beam method.

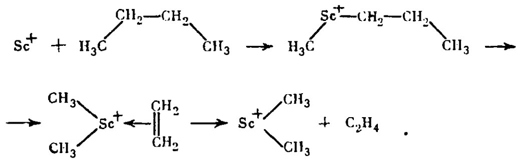
The reactions of Co^+ with cyclobutane, cyclopentane, and cyclohexane lead to the formation of dehydrogenation products and the products of the dissociation of the ring C–C bond according to Armentrout and Beauchamp.[42] For example, the reaction of Co^+ with cyclobutane proceeds as follows:



(17)

The gas-phase reactions of the FeH^+ ions, obtained by electron impact from 1,1-dimethylferrocene, with methane, ethane, and butane have been investigated for low kinetic energies of the ions.[62] It has been shown that methane and ethane do not react with FeH^+. The reaction of n-butane leads to the formation of the products of the insertion of FeH^+ in a C–H bond of the alkane, which agrees with data[57] for the analogous reactions of the FeD^+, CoD^+, and NiD^+ ion obtained by the reaction of metal ions with nitromethane or metal nitrite.

The reactions of Sc^+ ions having a kinetic energy of approximately 0.5 eV with alkanes ranging from propane to hexane in the gas phase have been recently investigated.[36] The Sc^+ ions were obtained by the thermal emission method at 2500 K. It was found that the reaction of propane with Sc^+ proceeds similarly to the reactions of alkanes with the Fe^+, Co^+, and Ni^+ ions. The main products are complexes of Sc^+ with propene (68%) and ethylene (27%). The reaction of n-butane leads to the formation of large amounts of the complex $Sc(C_2H_6)^+$ and ethylene respectively. Analysis of the thermochemical data led the authors[36] to the conclusion that the complex $Sc(C_2H_6)^+$ had the dimethylscandium structure. $Sc(CH_3)_2^+$ may be formed on insertion of Sc^+ to the terminal C–C bond of n-butane:



(18)

or to a C–H bond in the CH_2 group, which also leads to the formation of the dimethylethylene intermediate. The insertion of Sc^+ in a C–H bond leads to the formation of dehydrogenation products, which are, according to the authors' hypothesis, metallocyclobutane derivatives and not olefins and dienes bound in complexes as for other ions.

The gas-phase reactions of the Fe^+, Co^+, Ni^+, Cr^+, and Ti^+ ions with alkanes have also been investigated in other studies.[29,30] The metal ions were obtained by electron impact on the corresponding carbonyls (the Fe^+, Co^+, Ni^+, and Cr^+ ions) or the chloride (the Ti^+ ions). In their studies of the reactions of the Fe^+, Co^+, Ni^+, and Cr^+ ions with perdeuteriobutanes having the normal or isostructure, the authors concluded that the composition of the reaction products depends on the nature of the metal and the alkane. Table 2 presents the relative rate constants for the reactions of M^+ with butanes in the initial stage and shows that, in the presence of the Cr^+ ions, approximately 60% of the reaction steps involve the insertion of the metal in a C–D bond with subsequent formation of an olefin and a diene bound in complexes with Cr^+, while about 40% involve the insertion in the C_2–C_3 bond of butane with subsequent formation of ethylene. The insertion in the C_1–C_2 and C_3–C_4 bonds is not observed. The contribution by the reaction involving the insertion in the C_2–C_3 bond of n-butane increases sharply for Fe^+ and Co^+ with the corresponding fall of the rate of insertion in the C–H bonds. The formation of small amounts of complexes of propene with Fe^+ and Co^+ indicates the partial occurrence of the reaction also involving the C_1–C_2 (C_3–C_4) bonds. The reaction in which Fe^+, Co^+, and Ni^+ are inserted in a C–C bond is decisive for isobutane; the decomposition of the organometallic intermediate leads to the formation of a propene complex. The contribution by reactions involving the insertion in a C–H bond, which lead to an isobutene complex, is comparatively small.

In reactions of the Ni^+ ions with n-butane[29] and also with the C_4–C_7 alkenes, only insertion in a C–H bond takes place with subsequent β-decomposition of the organometallic compound and the formation of an olefin and hydrogen.

V. OXIDATIVE ADDITION OF OTHER ORGANIC COMPOUNDS TO TRANSITION METAL IONS

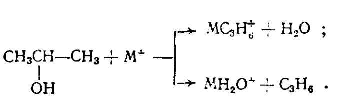
In conclusion we shall consider briefly the reactions of metal ions with derivatives of hydrocarbons containing various functional groups.

The gas-phase reactions of transition metal ions with aryl halides have been studied in relation to the interaction of the Fe^+ and Co^+ ions with CH_3I,[43] CH_3Br,[43] C_2H_5I,[44] and iso-C_3H_7Cl,[45] of the Ni^+ ions with CH_3I [44,45] and C_2H_5I,[45,45] of the Cr^+ ions with C_2H_5I,[44] and of the Fe^+ ions with C_6H_5Cl.[47] The above ions were obtained by electron impact on the corresponding metal carbonyls. The gas-phase reactions of Ti^+, obtained by laser radiation, with CH_3X (X = Cl, Br, or I), C_2H_5Cl, C_6H_5Cl, and $(CH_3)_2CHCl$ have been investigated.[46] The formation of the products of the oxidative addition to the C–Hal bond were observed in all cases. It is well known that RHal add analogously to active zerovalent metals in solution. The addition of alkenyl halides to $Ni(CO)_4$, leading to the formation of π-allyl derivatives,[63] and the addition of alkyl halides to zerovalent cobalt and other zerovalent metals[64,65] may serve as examples.

Table 2. The relative rate constants for the formation of the products of the reactions of M^+ with butanes.[30]

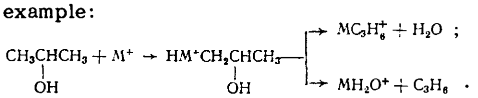
M^+	n-C_4D_{10}				iso-C_4D_{10}	
	$MC_2D_4^+$	$MC_3D_6^+$	$MC_4D_6^+$	$MC_4D_8^+$	$MC_3D_6^+$	$MC_4D_8^+$
Cr^+	0.22	0	0.16	0.16	0	0.09
Fe^+	0.53	0.07	0.04	0.04	0.46	0.09
Co^+	0.53	0.09	0	0.13	0.82	0.15
Ni^+	0.14	0.02	0	0.07	0.29	0.04

The gas-phase reactions of the Fe^+, Co^+, and Ni^+ ions, arising as a result of the electron impact on the corresponding metal carbonyls, with methyl, ethyl, and isopropyl alcohols have been studied.[44,45] The above ions induce the formation of mainly the products of oxidative addition to the C–OH bond with subsequent dehydration of the alcohols. $MC_2H_4^+$ ions were the main products of the reactions of the Fe^+, Co^+, and Ni^+ ions with ethyl alcohol, while approximately equal amounts of the $MC_3H_6^+$ and MH_2O^+ ions were found in the products of the reaction with isopropyl alcohol:



$$CH_3CH(OH){-}CH_3 + M^+ \rightarrow \begin{cases} MC_3H_6^+ + H_2O\ ; \\ MH_2O^+ + C_3H_6\ . \end{cases} \qquad (19)$$

In the given instance the reaction proceeds via the classical pathway involving the β-decomposition of the organometallic compounds. It is noteworthy that the analogous decomposition products can arise also when M^+ is inserted in a C–H bond, for example:



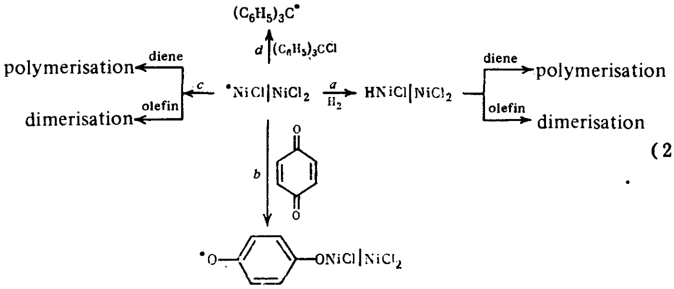
$$CH_3CH(OH)CH_3 + M^+ \rightarrow HM^+CH_2CH(OH)CH_3 \rightarrow \begin{cases} MC_3H_6^+ + H_2O\ ; \\ MH_2O^+ + C_3H_6\ . \end{cases} \qquad (20)$$

The gas-phase reactions of Fe^+ and Co^+ ions with acetaldehyde, acetone, ethyl methyl ketone, and isopropyl methyl ketone have been studied[49,50] as well as the reactions of Fe^+ ions with a series of other ketones—simple, mixed, unsaturated, and cyclic, also propionaldehyde and butyraldehyde.[49] The reaction of Co^+ ions with formaldehyde has been investigated.[50] Fe^+ ions have been obtained by the action of laser radiation,[49] while Co^+ ions have been generated by thermal ionisation.[50] The reactions involving Co^+ ions have been studied using a low kinetic energy of the ions. The composition of the products of the reactions with aldehydes and ketones depends on the nature of the carbonyl compound.

Thus acetone, formaldehyde and acetaldehyde give rise to only the $M(CO)^+$ ions—the products of oxidative addition to the C—C=O or H—C=O bonds. In the reactions with participation of ketones and aldehydes, there is a longer alkyl chain and the fraction of the products of oxidative addition to a C—H bond increases, while in the reactions with ketones having substituents at the α-carbon atoms and cyclic ketones there is an increase in the fraction of the products of oxidative addition to a C—C bond.

The gas-phase reactions of Fe^+ ions, obtained by the action of laser radiation, with ethers (dimethyl, diethyl, and di-isopropyl ethers, two mixed ethers—butyl methyl and isopropyl methyl ethers, and a cyclic ether—tetrahydrofuran) have been investigated.[49] The composition of reaction products depends on the nature of the ether. Thus dimethyl ether gives rise to only $FeCH_2O^+$ ions and correspondingly CH_4 (insertion in the C—O bond). The oxidative addition to the C—O bond predominates also for diethyl, di-iso-propyl, and isobutyl methyl ethers. For butyl methyl ether, the dehydrogenation reaction leading to the formation of $FeC_5H_{10}O^+$ and correspondingly H_2 is the dominant process.

It was already noted above that metal ions entering the gas phase under the influence of laser and especially electron irradiation are much more reactive than the ions of the same metals on the surfaces of catalysts and that even at room temperature hydrocarbons undergo more extensive reactions in the presence of such ions even at room temperature than in heterogeneous catalysis at not unduly high temperatures. It is noteworthy that metal subhalides, obtained on heating salts at 200—300 °C in a high vacuum and remaining in the matrix comprising halides, are to some extent analogous of metal ions. They are known to function as catalysts with selective activity in reactions with olefins at the usual temperatures. It has been shown[66,67] that small amounts of the ·NiCl species, detected by EPR in an $NiCl_2$ matrix, exhibit catalytic activity in diene polymerisation and ethylene dimerisation reactions at low temperatures.



(21)

The reactions via pathways *a* and *c* lead to the polymerisation of dienes and the oligomerisation of olefins, while along pathways *d* and *b* the system loses activity and triphenylmethyl and semiquinonoid radicals appear respectively. Analogous subhalides with catalytic activity in the above reactions arise when other metal halides are used.[66] One can also note that certain metal oxides, heated in a high vacuum at 400—500 °C for a long time, acquire the ability to catalyse deuterium exchange in hydrocarbons at low temperatures.[68] It may be that under the given conditions defects due to the formation of a small number of metal atoms in a more reduced state can arise in the catalyst matrix and are able to participate in the oxidative addition of hydrocarbons and deuterium.

The metal atoms formed on vaporisation in a high vacuum with their subsequent condensation in the hydrocarbon matrix[11] approach heterogeneous metallic catalysts as regards the character of their action on hydrocarbons although in this instance too isolated atoms are naturally more reactive than the atoms on the surface. It is well known that in the latter case the active centres are distributed on the crystal faces or in dislocation, where the metal atom retains a fairly large number of coordination vacancies and is able to pass to the oxidised state after combining with the hydrocarbon to form an organometallic intermediate.

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It follows from the data presented that, on coming into contact with an isolated metal atom at low temperatures, hydrocarbons undergo reactions analogous to their reactions in heterogeneous catalysis at higher temperatures. The reaction intermediates are in all cases organometallic compounds of transition metals, whose decomposition pathways have been thoroughly investigated in the temperature range 20—100 °C. Complex reactions of hydrocarbons (hydrogenation, dehydrogenation, skeletal isomerisation, hydrogenolysis, and deuterium exchange) can take place not only on an *ensemble* of metal atoms but also at an individual atom via stages involving the formation of organometallic intermediates arising as a result of the addition of the metal atom to C—H, C—C, and C—O bonds. The experimental data presented in this review are therefore of special interest for the understanding of the chemical nature of the elementary steps in heterogeneous catalysis.

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Norbornadienes in the Synthesis of Polycyclic Strained Hydrocarbons with Participation of Metal Complex Catalysts

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The advances achieved in recent years in the synthesis of polycyclic hydrocarbons, including those containing functional substituents, from norbornadiene and its derivatives using metal complex catalysts are surveyed. The homo- and codimerisation reactions of norbornadienes with olefins, dienes, and acetylenes, involving the $[2_\pi + 2_\pi]$-, $[2_\pi + 2_\pi + 2_\pi]$-, and $[4_\pi + 4_\pi]$-addition under the influence of transition metal complexes are examined. Data on the synthesis of norbornadiene trimers as well as the physicochemical and spectroscopic characteristics of a whole series of unique hydrocarbons are presented. The mechanisms of the reactions indicated are discussed.
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INTRODUCTION

Since the publication of Schauzer' review,[1] devoted to the problems of the synthesis of strained skeletal hydrocarbons from bicyclo[2.2.1]hepta-2,5-diene [norbornandiene (NBD)] (I) by methods involving metal complex catalysis more than ten years have elapsed. During this period, particularly in recent years, this field of chemistry has continued to develop vigorously. As a result, extensive theoretical and experimental data have accumulated, being concentrated mainly in publications and patents which are not readily accessible to many chemists. Even superficial analysis of the latest data on the synthesis of skeletal compounds indicates increasing importance of NBD as the key and fundamental monomer for the synthesis in a single stage of unique polycyclic strained hydrocarbons, among which NBD homodimers, trimers, and codimers are of greatest interest and practical value. The hydrogenated NBD dimers are widely used in the USA for the synthesis of high-density and high-energy multipurpose hydrocarbon rocket fuels.[2]

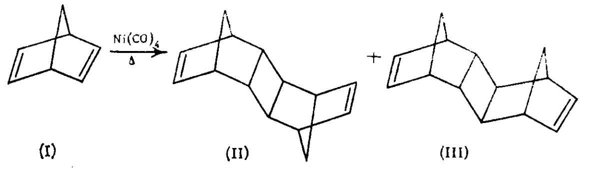
The transformations of norbornadienes into the corresponding cyclic dimers and trimers proceed as a rule under the influence of low-charge nickel, cobalt, iron, and rhodium complexes; manganese, chromium, titanium, palladium, and iridium compounds are used to a lesser extent. Active catalysts are obtained by reducing complexes of the above metals, soluble in organic solvents, with AlR_3, MgRR′, and their derivatives. Transition metal complexes containing electron-donating or electron-accepting ligands in their coordination spheres are used in many instances.

The literature data are described systematically in the present review on the basis of the nature of the central metal atom, since in the majority of cases the direction and structural selectivity of cyclo-oligomerisation of norbornadienes are determined by precisely this factor.

II. THE HOMODIMERISATION OF NORBORNADIENE UNDER THE INFLUENCE OF METAL COMPLEX CATALYSTS

1. Catalytic Systems Based on Nickel Compounds

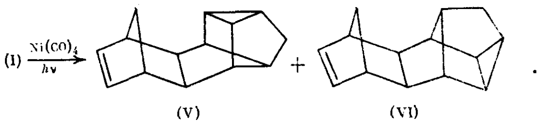
The cyclodimerisation of NBD via the $[2_\pi + 2_\pi]$addition mechanism was achieved for the first time by Bird et al.[3] using nickel tetracarbonyl as the catalyst. It was established subsequently[4-6] that $Ni(CO)_4$ promotes the formation of a mixture of isomers consisting of *endo,trans,endo*-pentacyclo[8.2.1.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]tetradeca-5,11-diene (II) and the *endo,trans,exo*-isomer (III) whose overall yield and composition depend significantly on the dimerisation conditions.



For example, when a mixture of NBD and $Ni(CO)_4$ with the ratio $Ni(CO)_4 : NBD = 1 : 100$ is refluxed for 6.5 h, a mixture of the isomers (II) and (III) is obtained in a quantitative yield in proportions of 1 : 3.[5] When the reaction is carried out in benzene, the content of the dimer (III) increases markedly to give (II) : (III) = 1 : 5.[6]

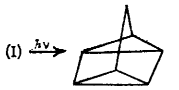
Complexes of unknown composition and structure, obtained when one of the three NBD $[2_\pi + 2_\pi]$dimers, namely *exo,trans,exo*-pentacyclo[8.2.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]tetradeca-5,11-diene (IV) or NBD itself is treated with nickel tetracarbonyl, drive the NBD cyclodimerisation reaction exclusively towards the formation of the isomer (III).[5] The yield of compound (III) varies from 69 to 91% depending on the conditions used in preparation of the complexes indicated.

The direction of the $[2_\pi + 2_\pi]$reaction changes when the NBD cyclodimerisation is carried out in the presence of catalytic amounts of $Ni(CO)_4$ with simultaneous UV irradiation. The $[2_\pi + 2_\pi + 2_\pi]$dimers (V) and (VI) are formed exclusively in these experiments in an overall yield of ~11%: [5]



(V) (VI)

Unfortunately, the authors[5] hardly discussed the mechanism of this interesting reaction. Under the conditions of UV irradiation, quadricyclane (QC) is probably formed initially and readily dimerises to the cyclic dimers (V) and (VI) under the influence of low-charge nickel carbonyl complexes containing in the coordination sphere NBD molecules together with carbon monoxide:



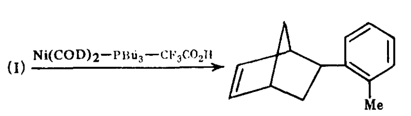
QC

This mechanisms has been confirmed by the results of studies[7-9] according to which quadricyclane is converted into $[2_\pi + 2_\pi + 2_\pi]$dimers and codimers in fairly high yields in the presence of complex catalysts based on nickel, palladium, and rhodium compounds.

The replacement of $Ni(CO)_4$ by $Ni(CO)_2(PPh_3)_2$ in the photoinitiated NBD cyclodimerisation reaction leads to the formation of the *exo,trans,exo*-isomer (IV) with a high selectivity.[10]

Cyclisation of the $[2_\pi + 2_\pi]$ type remains the principal pathways in the NBD dimerisation reaction using as catalysts zerovalent nickel complexes containing olefin, diene, and organophosphorus ligands in the coordination sphere. For example, $Ni(COD)_2$ (where COD = cyclo-octa-1,5-diene) converts NBD into the *exo,trans,exo*-dimer (IV) with a selectivity of 96.5%.[11] When triphenylphosphine is introduced into the composition of $Ni(COD)_2$, the selectivity in the formation of the dimer (IV) falls to 66.1% owing to the increase of the fraction of the *endo,trans,exo*-isomer (III).[12]

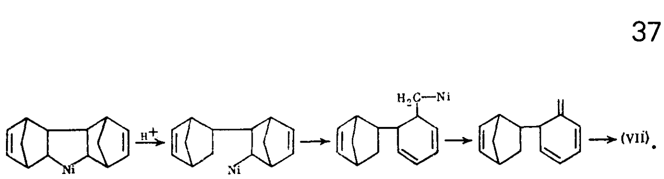
The dimerisation of NBD proceeds quite differently in the presence of the $Ni(COD)_2$–PBu_3 catalytic system promoted by CF_3CO_2H;[12] the only reaction product is then 5-exo-(o-tolyl)norborn-2-ene (VII), whose yield is 30%:



(VII)

Without the addition of trifluoroacetic acid, a mixture of NBD $[2_\pi + 2_\pi]$dimers (II)–(IV) was obtained in a yield of 60%, but the isomeric composition was not investigated.[12]

An analogous conversion of NBD into compound (VII) takes place in the presence of complexes of the type $NiX_2.PBu_3$ in solution in isopropylamine.[13] The introduction of $NaBH_4$ into the nickel–phosphine complex makes it possible to increase the yield of the product (VII) to 81.5%.[13] According to the authors,[13] the reaction proceeds via a mechanism whose first stage involves the activation of NBD via coordination with the central metal atom in the formation of the metallocyclic compound (VIII). In the presence of CF_3COOH, the latter undergoes a series of consecutive reactions leading to the formation of the dimer (VII):



(VIII)

Acrylonitrile complexes, which have been studied in detail by Schrauzer and Eichler[14] and which catalyse the dimerisation of NBD predominantly to the *endo,trans,exo*-isomer (III), play an important role in the series of nickel-containing catalysts of the dimerisation of NBD via the $[2_\pi + 2_\pi]$ addition mechanism.

The introduction of phosphines into acrylonitrile complexes of nickel increases the overall yield of dimers, which consist as a rule of the isomers (III) and (IV), to 80%, the selectivity in the formation of the isomer (III) being 98%.[14,15] It has been established that the ratio of the concentrations of the dimers (III) and (IV) is correlated with the electron density at the nickel atom: with increase of the effective charge on the central metal atom, the fraction of the isomer (III) also rises. Unfortunately, these data are insufficient to establish the detailed mechanism of the NBD cyclodimerisation reaction.

Thus the cyclodimerisation of NBD under the influence of nitrile complexes of nickel proceeds with the preferential formation of the *endo,trans,exo*-isomer (III) regardless of the nature and structure of the organophosphorus activator-ligands. With increase of reaction temperature, the fraction of this product in the reaction mixture increases.

Catalytic systems based on $Ni(CN)_2$ and phosphinites, phosphonites or phosphites are active in the cyclodimerisation of NBD also in the absence of a reducing agent.[16,17] For example, the catalyst prepared from $Ni(CN)_2$ and $PPh_2(OBu)$ converts NBD into a mixture of three possible $[2_\pi + 2_\pi]$ isomers (II)–(IV) in proportions of 62 : 5 : 33 and an overall yield of ~90%.

Under the reaction conditions, catalytically active nickel complexes are apparently formed on reduction of Ni^{2+} ions by the initial diene or the dimerisation products to Ni^+ or Ni^0. For example, in the presence of the complex $[Ni(acac)_2.(IV)]$, NBD is converted into the dimer (IV) in an overall yield of 53%.[4]

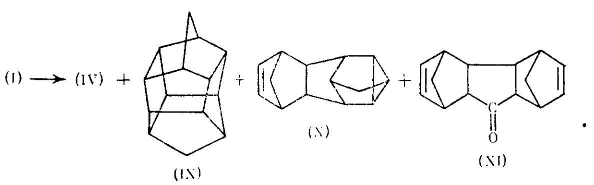
It is noteworthy that two- and three-component catalytic systems prepared from $Ni(acac)_2$, $AlEt_3$, and PPh_3, are much more productive than other known nickel-containing catalysts whose efficiency does not exceed 50–100 moles of the required product per gramme-atom of nickel.[4,11,18-23] Furthermore, the catalysts indicated are active in the dimerisation of NBD over a wide temperature range (20–200 °C) and effect the reaction both in the presence of solvents and in their absence. The yield of the mixture of dimers (II)–(IV) then varies from 40 to 87%. There is no doubt that these catalysts are extremely promising for the industrial application of the process.

The foregoing permits the conclusion that nickel-containing complex catalysts catalyse the cyclodimerisation of NBD via the $[2_\pi + 2_\pi]$ mechanism with formation of pentacyclic hydrocarbons regardless of the nature of the anion attached to the metal atom and also of the structure of the ligands and the reaction conditions.

2. Iron-containing Catalysts in Norbornadiene Dimerisation Processes

Iron-containing catalysts, which are frequently used in NBD dimerisation processes, are characterised, in contrast to the nickel catalyst, by a wider spectrum of their activity. Depending on the nature of the selective complex (ligand environment, oxidation state of iron) and the reaction conditions, they successfully effect all three variants of the NBD cyclodimerisation via the $[2_\pi + 2_\pi]$-, $[2_\pi + 2_\pi + 2_\pi]$-, and $[4_\pi + 4_\pi]$-addition mechanisms.

The formation of the NBD dimer in the presence of $Fe(CO)_5$ was first observed as early as 1959,[24] but the product obtained could not be identified. The above report[24] stimulated studies on the cyclodimerisation of NBD with participation of iron complexes. The complexes $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ were tested as catalysts of the dimerisation of NBD.[25-27] It was found that all the iron carbonyls exhibit catalytic activity in the NBD cyclo-oligodimerisation and lead to the formation of a complex mixture of hydrocarbons and carbonyl compounds. The dimers (IV), (IX), and (X) and the polycyclic ketones (XI), whose overall yields do not exceed 20%, were detected in the products.



The dimers (IV) and (IX) were identified as *exo,trans,exo*-pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene and heptacyclo[6.6.0.0^{2,12}.0^{3,7}.0^{4,11}.0^{5,9}.0^{11,14}]tetradecane, but final evidence for the correctness of these structures was obtained somewhat later.[28,29] The authors were unable to establish the structure of the hexacyclic dimers (X).

Iron nitrosyl complexes, distinguished by a high activity, productivity, and selectivity of their action, have been used[30] for the cyclodimerisation of NBD. The $[2_\pi + 2_\pi]$dimers (III) and (IV) were obtained exclusively in ~98% yield when $Fe(CO)_2(NO)_2$ was used.[30,31]

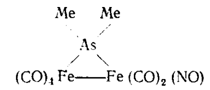
The study of Jolly et al.[30] initiated the systematic search for and development of highly active catalysts for the selective cyclo-oligomerisation of NBD. A whole series of iron nitrosyl complexes were obtained and investigated in the course of several years and certain characteristics of their action in NBD reactions were discovered.[32-43]

In particular, it was established that the catalytically active species responsible for the formation of the NBD dimer molecules was the coordination-unsaturated complex $Fe(NO)_2^*$,[30,31,39,40,42] which is probably formed under the reaction conditions when nitrosyl ferrates interact with NBD or its dimers.

Similar results were obtained in the electrochemical and chemical reduction of $[Fe(NO)_2Cl]_2$ in the presence of PPh_3.[39,40,42] The complex $[Fe(NO)_2Cl]_2$ is converted quantitatively into $Fe(NO)_2^*$ and the compounds $Na[Fe(CO)_3NO]$ and $Hg[Fe.(CO)_3NO]_2$ are converted into $Fe(CO)_2(NO)_2$, which the authors believe readily dissociates into CO and $Fe(NO)_2^*$.[44] Regardless of the structure and nature of the initial complex, only the $[2_\pi + 2_\pi]$dimers (III) and (IV) are formed in the presence of the systems indicated.

These results show that the mechanism of the cyclodimerisation of NBD under the influence of different iron nitrosyl complexes remains unchanged. The nature of the reductant hardly affects the yield of the dimers (III) and (IV) and the reaction selectivity. When powdered zinc is used as the reducing agent, the degree of conversion of NBD depends markedly on the nature of the solvent. Thus high yields of dimers (93%) have been obtained in acetone and tetrahydrofuran (THF). When the reaction is carried out in toluene, methanol, and acetonitrile, the yield of dimers falls.[38] In the presence of the $[Fe(NO)_2Cl]_2/AgBF_4$ catalytic system, best results are obtained in the dimerisation of NBD in pure methylene chloride. The selectivity in the formation of the dimer (IV) then amounts to 94% for a degree of conversion of NBD of 76%. It is noteworthy that $AgBF_4$ is the most effective promoting agent among the cocatalysts tested.

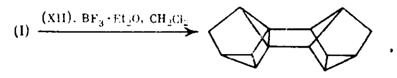
A high catalytic activity and selectivity in the reaction of the cluster compound (XII), which belongs to be class of iron carbonyl nitrosyl complexes considered, has been observed recently. At 60 °C in benzene, it converts NBD quantitatively into the *exo,trans,exo*-dimer (IV).[45,46]



$$(CO)_3Fe\overset{AsMe_2}{\text{——}}Fe(CO)_2(NO)$$

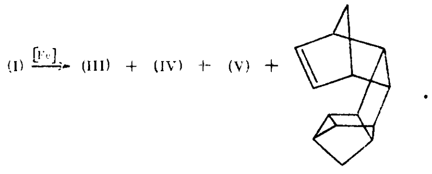
(XII)

A unique instance of a change in the selectivity in the dimerisation of NBD has been observed when an equimolar amount of $BF_3.OEt_2$ was added to compound (XII).[45] The only reaction product is the dimer (XIII), namely *endo,endo*-heptacyclo[8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}]tetradecane ("Binor-S"), formed via $[4_\pi + 4_\pi]$cycloaddition:



(XIII), (100%)

An author of several patents,[4,19,47] who used the $Fe(acac)_3$–$AlEt_3$ and $Et_2Al(OEt)$ catalytic systems for the dimerisation of NBD, achieved major successes in the synthesis of pentacyclic and hexacyclic NBD dimers. Iron acetylacetonate, reduced with triethylaluminium, catalyses the dimerisation of NBD with formation of a mixture of four hydrocarbons (III), (IV), (V), and (XIV):



(XIV)

The hexacyclic isomers (V) and (XIV) have been identified by Scharf et al.[48] The ratio of the isomers formed and the overall yield depend on the reaction conditions and the method of preparation of the catalyst. The addition of the olefin to the catalyst prepared at 0 °C and heating at 40 °C for 20 h result in the formation of a mixture of dimers of the following composition in a yield up to 97%: 63.6% (III), 24.3% (IV), and 12.1% [(V) + (XIV)].[4] The simultaneous addition of NBD solutions of $Fe(acac)_3$ and $AlEt_3$ to the reactor heated to 140–200 °C makes it possible to obtain mixtures of the isomers (III)–(V) and (XIV) containing 64–72% of hexacyclic hydrocarbons.[49-51]

The use of 1,2-bis(diphenylphosphino)ethane (BPE) and replacement of triethylaluminium by diethylaluminium chloride in the $Fe(acac)_3$–AlR_3 catalytic system make it possible to increase the selectivity in the formation of the *exo,exo-dimer* (VI) to 80–90%,[52,53] while the addition of triphenylphosphine alters the direction of the reaction towards the preferential formation of the *endo,endo*-isomer (XIV).[54]

Biscyclo-octatetraeneiron and the catalytic system obtained by reducing $FeCl_3$ with isopropylmagnesium chloride catalyse the dimerisation of NBD to the isomers (IV) and (VI) with the preferential formation of the latter.[55] When $FeCl_3$ is reduced with triethylaluminium or sodium, a catalyst active in the $[2_\pi + 2_\pi + 2_\pi]$cycloaddition is also obtained.[56]

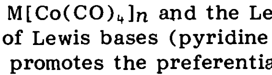
Thus, among the iron-containing NBD dimerisation catalysts investigated, the highest activity and productivity (up to 1000 moles of NBD converted per gramme-atom of iron) is shown by catalytic systems of the Ziegler–Natta type: $Fe(acac)_3-AlR_3(AlEt_3)$ or $Et_2Al(OEt)$. They are superior to the analogous nickel catalysts because of the consistently high yield of the dimers (70–90%) and the better reproducibility of the results.

3. Dimerisation of Norbornadiene in the Presence of Cobalt Catalysts

Cobalt compounds exhibit an exceptionally high catalytic activity in the cyclo-oligomerisation reactions of NBD. The first report of their use for the dimerisation of NBD dates back to 1961;[26] however, the above communication does not contain experimental details. In a classical study[28] devoted to the determination of the stereochemistry of the NBD $[2_\pi + 2_\pi]$ dimers, it was later shown that $Co_2(CO)_8$ combined with PPh_3 converts NBD into a mixture of two $[2_\pi + 2_\pi]$ isomers: the *endo,trans,exo*-isomer (III) and the *exo,trans,exo*-isomer (IV) with a (III) : (IV) ratio of 1 : 10.

Interesting results have been obtained in the dimerisation of NBD in the presence of the $Co(CO)_3(NO)$ catalyst isoelectronic with the complex $Fe(CO)_2(NO)_2$.[30] It was found that the former effects $[2_\pi + 2_\pi]$cycloaddition. In these experiments $[2_\pi + 2_\pi + 2_\pi]$dimers were formed together with compound (IV). The quantitative composition of the hexacyclic hydrocarbons (V) and (XIV) is not stated in the above communication. Furthermore, the dimer (IV) can be obtained with a selectivity up to 98% when the complex $[Co(NO)_2Cl]$ or $[Co(NO)_2Br]$, promoted with $AgPF_4$ or $NaBPh_4$, is used as the catalyst.[32,34–36].

In studies[1,57,58] of the catalytic properties of cobalt compounds in the cyclo-oligomerisation reactions of cyclic olefins and dienes, it has been observed that complexes of the type $M[Co(CO)_4]_n$ (where M = Zn, Cd, or Hg) effect the stereospecific dimerisation of NBD via the $[4_\pi + 4_\pi]$mechanism with formation of "Binor-S" (XIII) (in 95% yield). The structure of compound (XII) could not be demonstrated for a long time. However, the specific synthesis by the Wolff–Kishner reduction of the diketone (XV) [59,60] made it possible to establish finally that the dimer (XIII) has, as already suggested,[57,58] the structure of *endo,cis,endo*-heptacyclo$[8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}]$tetradecane.

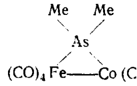


(XV) → (XIII) .

In order to carry out the cyclodimerisation of NBD to compound (XIII) under the influence of the catalysts investigated, it is essential to have cocatalysts of the type BF_3, SbF_3, $AlBr_3$, and $BF_3.OR_2$, whose greatest efficiency is achieved when the ratio of $M[Co(CO)_4]_n$ and the Lewis acid is 1 : 8. The introduction of Lewis bases (pyridine and triethylamine) into the catalysts promotes the preferential formation of pentacyclic and hexacyclic dimers.[57,61]

Dinuclear and polynuclear cobalt catalysts of the cyclodimerisation of NBD to the penta-, hexa-, and hepta-cyclic dimers (III), (IV), (V), (XIII), (XIV) were subsequently obtained and investigated. The activity and selectivity of the action of these catalysts depend greatly on the nature of the anion in the coordination sphere of the central metal atom and also on the structure of the cocatalyst (Lewis acid), the nature of the solvent, and the reaction conditions.[57,59,62–69] For example, the trinuclear complex (XVI) converts NBD into a 1 : 1 mixture of the dimers (XIV) and (XIII). When the Lewis acid $BF_3.OEt_2$ is introduced into the catalyst, the process can be directed towards the formation of compound (XIII) (in ~100% yield):[45,46]

$$(IV) \xleftarrow{(XVI)} (I) \xrightarrow{(XVI)+BF_3\cdot OEt_2} (XIII) .$$



(XVI)

The study of the kinetics of the cyclodimerisation of NBD to "Binor-S" (XIII) in the presence of the dinuclear catalyst $(Ph_2C_2)Co(CO)_6$ established that the reaction is first order with respect to the catalyst and that the activation energy is ~38.58 kcal mol^{-1}.[63]

Systems obtained by reducing $Co(acac)_2$ with organoaluminium compounds have a high catalytic activity in the NBD dimerisation reactions. The dimers (III) (29%) and (IV) (62%) and the $[2_\pi + 2_\pi + 2_\pi]$dimers (X) (yield 9%) of unknown composition are formed in the presence of the $Co(acac)_2-AlEt_3$ system:[4]

$$(I) \longrightarrow \underset{29\%}{(III)} + \underset{62\%}{(IV)} + \underset{9\%}{(X)} .$$

The authors note[53] that the direction of the NBD cyclodimerisation can be completely altered by employing the three-component $Co(acac)_2-1,2$-bis(diphenylphosphino)ethane–Et_2AlCl system as the catalyst. In this case the dimer (VI) is formed quantitatively. The replacement of the bisphosphine by PPh_3 leads to the formation of the isomer (XIII).[61]

Thus the cobalt-containing catalysts are extremely effective in the synthesis of the heptacyclic NBD dimer "Binor-S", which has found extensive applications in the synthesis of diamond-like structures.

4. Complexes Based on Rhodium in the Norbornadiene Dimerisation Processes

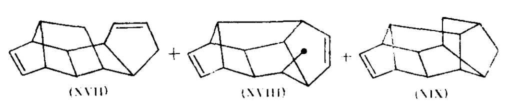
It is noteworthy that rhodium catalysts are distinguished by a low selectivity in the NBD dimerisation processes and as a rule lead to the formation of a complex mixture of polycyclic hydrocarbons. The fundamental studies on the application of rhodium-containing catalysts in the NBD dimerisation reactions have been carried out by Katz and co-workers (Columbia University). These investigators were able to isolate and identify a whole series of NBD dimers and trimers with the aid of modern physicochemical methods. Unfortunately, they investigated and tested only a limited number of rhodium complexes capable of effecting the dimerisation or trimerisation of NBD.

For example, the dimerisation of NBD in the presence of the 5% Rh/C catalyst takes place relatively selectively; NBD is then converted into a mixture of the isomers (IV), (V), and (XIV) in 53% yield:[71]

$$(I) \xrightarrow{Rh/C} \underset{4\%}{(IV)} + \underset{84\%}{(V)} + \underset{12\%}{(XIV)}$$

In the presence of Wilkinson's complex $[Rh(PPh_3)_3Cl]$, the dimerisation of NBD is accompanied by the skeletal isomerisation of the *exo,endo*-hexacyclo$[9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}]$tetradec-12-ene (V) to the hydrocarbons (XVII), (XVIII), and (XIX):[29,72]

$(I) \longrightarrow (V) + (IX) +$



(XVII) + (XVIII) + (XIX) .

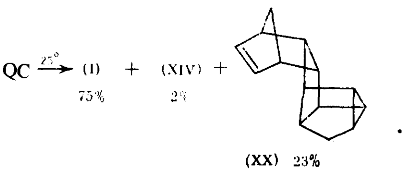
The introduction of an additional amount of PPh_3 into the complex $[Rh(PPh_3)_3Cl]$ hardly affects the direction of the dimerisation reaction,[29] but the composition of the cyclodimerisation products changes appreciably under these conditions.

The rhodium catalysts obtained by reducing $[Rh(PPh_3)_3Cl]$ with Et_2AlCl or $EtAlCl_2$ convert NBD into "Binor-S" (XIII) in an almost quantitative yield.[73] Analogous results have been obtained using catalytic systems with a fairly complex structure: $Rh(NBD)_2PF_6–PPh_3$, $P(OPh)_3]$ or $[Rh_4(CO)_{12}–BF_3.OEt_2]$.[64,71] The dimerisation of NBD under the influence of complexes of the type of $Rh(NBD)_2BF_4$ results in the formation of mainly the hexacyclic dimers (V), (VI), and (XIV):[75]

$$(I) \xrightarrow{[Rh]} \underbrace{(V) + (VI)}_{60\%} + \underset{10\%}{(XIV)} \;.$$

A selective method of synthesis of the dimer (V) using rhodium catalysts has been proposed by Japanese workers.[13] The authors used the catalytic system $Rh(C_8H_{14})Cl–CF_3CO_2H$ (C_8H_{14} = cyclo-octene; Rh : CF_3COOH = 1 : 4).

It is noteworthy that, in contrast to other catalysts, the rhodium complexes are capable of converting quadricyclane (QC) into the corresponding NBD dimers. For example, when quadricyclane is treated with the carboxylate complex $[Rh(NBD)AcO]_2$ in methylene chloride at room temperature, NBD is mainly formed together with a small amount of the hexacyclic dimers (XIV) and (XX). The *endo,exo*-isomer (XX) has been obtained by a catalytic process only under the conditions indicated:[7]



It is believed[76] that the initial NBD plays the role of a reductant in relation to the rhodium(II) carboxylate complexes. According to these workers,[76] the NBD dimerisation process begins only after the conversion of rhodium(II) into rhodium(I) under the influence of NBD. The rhodium(I) complex formed under these conditions is an effective catalyst of the $[2_\pi + 2_\pi + 2_\pi]$cyclo-dimerisation of NBD. It has been noted[74] that the activity of the rhodium trifluoroacetate complexes is higher by an order of magnitude than that of the acetate complexes. Fairly active catalysts of the dimerisation of NBD to a mixture of compounds(V) and (XIV) have been obtained by reducing $Rh(acac)_3$ with the organoaluminium compounds Et_2AlCl and $EtAlCl_2$.[77]

The above studies exhaust the available literature data on the use of rhodium complexes in the cyclodimerisation reactions of NBD. It follows from the results presented above that catalysts based on rhodium salts and modified by Lewis bases or acids have universal properties and make it possible to obtain seven of the nine of the known NBD dimers. However, only a limited number of rhodium complexes have so far been investigated and tested as catalysts of the cyclo-oligomerisation of NBD and its derivatives can lead to the creation of new highly effective catalytic systems for the selective synthesis of polycyclic hydrocarbons with the unique structure from NBD and its derivatives.

5. Dimerisation of Norbornadiene in the Presence of Other Catalysts

Apart from the nickel-, iron-, cobalt-, and rhodium-containing catalysts, systems based on chromium, manganese, palladium, and iridium compounds as well as phenyl-lithium are used for the cyclodimerisation of NBD.[9,78,80,164]

In particular, the photolysis of chromium hexacarbonyl in solution in NBD leads to the formation of a mixture of pentacyclic hydrocarbons consisting of the *endo,trans,endo*-(II), *endo,trans,exo*-(III), and *exo,trans,exo*-(IV) isomers in

The physicochemical properties of the norbornadiene dimers.

Compound	B.p., °C/*p*, mmHg	M.p., °C	n_D^{20}	d_4^{20}	(M.p.)^h, °C	$(d_4^{20})^h$	Refs.
(II)	75/0.2	92—93	1.516*	—	99—102	—	[28, 84]
(III)	75/0.2	—25	—	—	38—39	—	[28, 84]
(IV)	237/760	67—68	1.518**	—	63.8±0.6	0.983***	[28, 84, 85]
(V)	117—119/10	14—16	1.5457	1.092	21.1±0.7	1.068****	[48, 85]
(VI)	—	—	—	—	12.3±0.2	1.077	[85]
(IX)	—	165—165.5	—	—	—	—	[25]
(XIII)	73/1—2	65—65.5	—	—	—	—	[57]
(XIV)	122/10	—23+—21	1.5521	1.105	8.0±0.2	1.089	[48, 85]
(XX)	121—122/10	—	1.5446	1.09	—	—	[48]

Notation: B.p. = boiling point; *p* = pressure, M.p. = melting point, d_4^{20} = density, n_D^{20} = refractive index, and (M.p.)^h and $(d_4^{20})^h$ are the values for the hydrogenated dimer.
*At 94 °C; **at 79 °C; ***at 70 °C; ****at 30 °C.

Note. Numbers in square brackets denote references (Ed. of Translation).

proportions of 1.4 : 1.0 : 1.8 respectively.[78] According to Carbonaro et al.,[79] manganese catalysts are active in the NBD cyclodimerisation reaction, but the authors do not present detailed data on the yield and composition of the dimers formed.

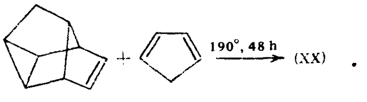
The possibility of using palladium complexes for the selected conversion of quadricyclane (QC) into a mixture of the dimers (V) and (VI) in a high yield have been demonstrated in a recent communication:[9]

$$\mathrm{QC} \xrightarrow{\mathrm{Pd_2(DBA)_3(CHCl_3)}} \mathrm{(V)} + \mathrm{(VI)}\ ;$$

$$\mathrm{DBA} = \mathrm{PhCH{=}CH{-}CO{-}CH{=}CHPh}\ .$$

Phenyl-lithium reacts with bicyclo[2.2.1]hepta-2,5-diene in ether and gives rise to a mixture of two NBD dimers whose yield depends on the ratio of the initial reactants.[80]

The NBD dimer (XX), which is difficult to synthesis, can be obtained in ~77% yield from deltacyclene (XXI) and cyclopentadiene by the Diels–Alder reaction:[48,81]



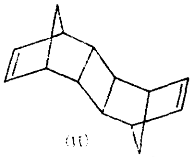
(XXI)

6. The Physicochemical Properties of Norbornadiene Dimers

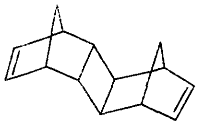
Out of the fourteen theoretically possible NBD dimers, capable of being formed only as a result of bond cyclisation via reactions of the $[2_\pi + 2_\pi]$, $[2_\pi + 2_\pi + 2_\pi]$, and $[4_\pi + 4_\pi]$ types, nine have been actually synthesised. The physicochemical characteristics of these compounds as well as their hydrogenated derivatives are presented in the Table. The formation of other NBD dimers, namely (XVIII) and (XIX), which are the products of further reactions (skeletal rearrangement) of the hexacyclic isomers, has been noted in a series of studies.[29,72]

The theoretically possible NBD dimers are presented below.†

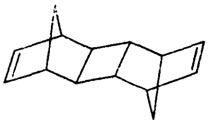
(1) Pentacyclic hydrocarbons: pentacyclo[$8.2.1.1^{4,7}.0^{2,9}.0^{3,8}$]deca-5,11-dienes—the products of the NBD $[2_\pi + 2_\pi]$dimerisation:



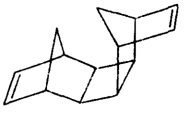
(II)
endo, trans, endo



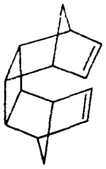
(III)
endo, trans, exo



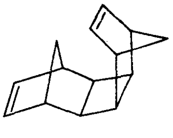
(IV)
exo, trans, exo



(XXII)
exo, cis, exo
(not obtained)

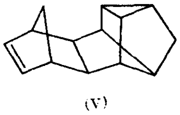


(XXIII)
endo, cis, endo
(not obtained)

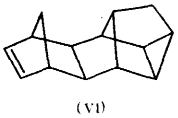


(XXIV)
exo, cis, endo
(not obtained)

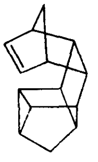
(2) Hexacyclic hydrocarbons: hexacyclo[$9.2.1.0^{2,10}.0^{3,8}.0^{4,6}.0^{5,9}$]tetradec-12-enes—the products of the NBD $[2_\pi + 2_\pi + 2_\pi]$dimerisation:



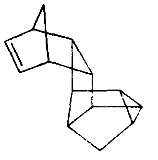
(V)
exo, endo



(VI)
exo, exo



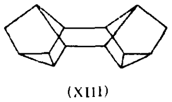
(XIV)
endo, endo



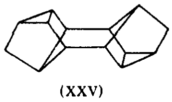
(XX)
endo, exo

(3) Heptacyclic hydrocarbons—the products of the NBD $[4_\pi + 4_\pi]$dimerisation.

(a) Heptacyclo[$8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}$]tetradecanes:

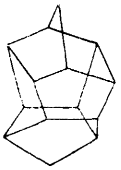


(XIII)
endo, cis, endo
("Binor-S")



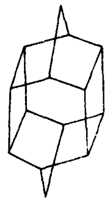
(XXV)
endo, trans, endo
(Binor-A obtained by the isomerisation of Binor-S)

(b) Heptacyclo[$6.6.0.0^{2,12}.0^{3,7}.0^{4,11}.0^{5,9}.0^{10,14}$]tetradecane:



(IX)

(c) Heptacyclo[$9.3.0.0^{2,5}.0^{5,13}.0^{4,8}.0^{6,10}.0^{9,12}$]tetradecane:



(XXVI)
(not obtained)

Owing to the complexity of their structures, the determination of the stereochemistry of the NBD dimers required much effort by investigators. In analysing the available data, one must note that the most convincing and unambiguous conclusions concerning the structure of polycyclic hydrocarbons can be obtained using the entire range of modern spectroscopic methods.[28,29] Studies of the ^{13}C NMR spectra of all the known NBD dimers and their hydrogenated derivatives are therefore of undoubted interest and practical value.[87]

III. THE HOMO- AND CO-DIMERISATION OF SUBSTITUTED NORBORNADIENES

The early studies on the catalytic reactions of substituted NBD includes those on the homocyclodimerisation of 1-, 2-, and 7-methylbicyclo[2.2.1]hepta-2,5-dienes under the influence of the complexes $\mathrm{Ni[P(OPh)_3]_4}$ and $\mathrm{Fe(acac)_3{-}AlEt_3}$.[20,21,49,51] The authors believe that mainly $[2_\pi + 2_\pi]$- and $[2_\pi + 2_\pi + 2_\pi]$-dimers are formed in these experiments, but the

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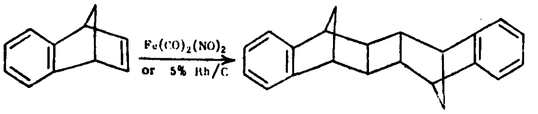
† The names of compounds (II)–(VI), (IX), (XIII), (XIV), (XX), and (XXII)–(XXVI) have been revised in accordance with new recommendations.[82,83]

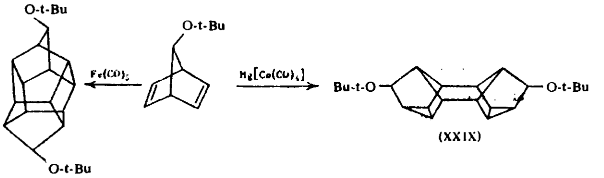
individual products were not isolated and identified. Unfortunately, the above communications do not contain data on the basis of which one could estimate and compare the activities of the substituted NBD in reactions catalysed by transition metal complexes.

Regardless of the nature of the catalyst [5% Rh/C or $Fe(CO)_2(NO_2)$], benzonorbornadiene is converted exclusively into compound (XXVII): [81,92]



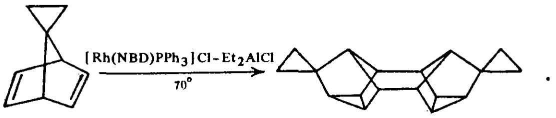
(XXVII), *exo, trans, exo*

According to Ennis et al., [86] 7,14-dimethylheptacyclo-$[8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}]$tetradecane is formed on dimerisation of 7-methylnorbornadiene under the influence of the catalyst $(NBD)_2Co_2(CO)_4$–$BF_3.OEt_2$. [85] It was established that the introduction of the fairly bulky t-butoxy-group in the 7-position, which is most remote from the double bond, does not have an appreciable influence on the stereospecificity of the dimerisation reaction. Depending on the nature of the catalyst, either 6,13-di-t-butoxyheptacyclo-$[6.6.0^{2,12}.0^{3,7}.0^{4,11}.0^{5,9}.0^{11,14}]$tetradecane (XXVIII) or the disubstituted "Binor-S" (XXIS) is formed: [60,88–90]



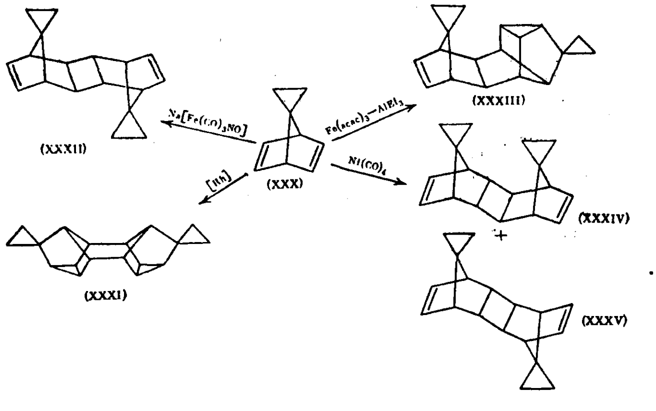
(XXIX)

The reactions of 7,7-disubstituted NBD, namely spiro{bicyclo[2.2.1]hepta-2,5-diene-7,1^1-cyclopropane} (XXX), were investigated for the first time in fair detail in a number of studies. [91,92,94] The [4_π + 4_π]cyclodimerisation of compound (XXX), achieved recently with formation in a single stage of the nonacyclic compound (XXXI), is evidence for the exceptional effectiveness of the method involving metal complex catalysis in the synthesis of strained skeletal hydrocarbons.[91]

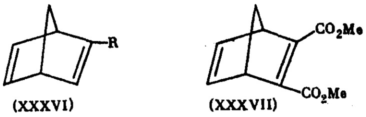


(XXX) (XXXI), 95%

It has been established [93–95] that the reactivity of compound (XXX) in cyclodimerisation reactions is not inferior to that of NBD, for which it has been possible to obtain the [2_π + 2_π]- and [2_π + 2_π + 2_π]dimers:



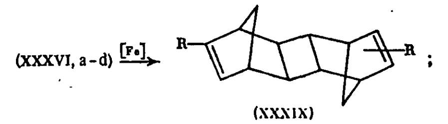
The results of the study of the catalytic homo- and codimerisation of 2- and 7-substituted NBD (XXVI, a–g), (XXX), and (XXXVII) in the presence of the complexes $Fe(CO)_2(NO_2)$ and $Na[Fe(CO)_3(NO)]$ were published for the first time by Dzemilev and co-workers: [93,95]



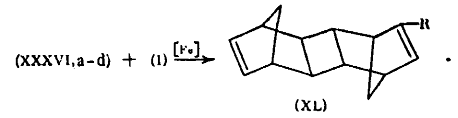
(XXXVI) (XXXVII)

R = Me(a), CH_2OH(b), CH_2OMe(c), CO_2Me(d), Cl(e), CHO(f), CH_2OAc(g)

It was found that only the dienes (XXXVI, a–d) and (XXX) are involved in the homodimerisation reaction and in codimerisation with NBD, the products being the 5(6),11-disubstituted and 5-monosubstituted *exo,trans,exo*-pentacyclo-$[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]$tetradeca-5,1-dienes (XXXIX) and (XI):



(XXXIX)



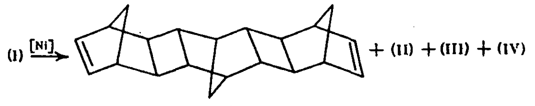
(XL)

The selectivity in the formation of the *exo,trans,exo*-dimers is fairly high (≥91%).

The substituted NBD (XXXVI, e–g) do not form homodimers. The reduced reactivity of the dienes (XXXVI, e–g) may be caused by the change in the energy of the π orbitals as a function of the nature of the substituent. However, the results obtained in a study [95] of 2- and 7-substituted NBD by photoelectron spectroscopy permitted a quantitative demonstration that the energy of the π orbitals of the 1,4-diene system in substituted NBD varies only slightly. The authors [95] therefore assume that the low reactivity of compounds (XXXVI, e–g) can be accounted for by their involvement in the formation of coordination-saturated complexes with the central metal atoms, which are relatively inactive in homo- and co-dimerisation processes. This conclusion was confirmed by the fact that even smaller amounts of the above monomers added to the reaction medium deactivate the catalyst and suppress the dimerisation of both NBD and of the substituted NBD (XXXVI, a–d).

IV. THE SYNTHESIS OF NORBORNADIENE TRIMERS

Up to 1983, only two norbornadiene trimers had been obtained and isolated in low yields from a mixture of polycyclic products of the reaction of NBD under the influence of metal complex catalysts based on nickel and rhodium compounds. [4,9–11,18,29,71,72,75,76] For example, in the presence of $Ni(PPh_3)_4$, $Ni(CO)_2$, $(PPh_3)_2$, or Ni^0–PPh_3, NBD is converted into *exo,trans,exo,trans,exo*-octacyclo$[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]$heneicosa-5,14-diene (XLI) in ~5% yield: [4,10,11,18]

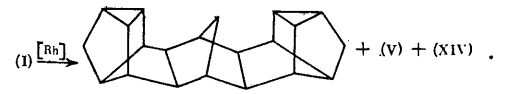


(XLI)

According to Ref.4, the yield of compound (XLI) increases to 40% when the cyclotrimerisation of NBD is carried out in dioxan in the presence of catalytic amounts of $Ni(COD)_2$. Unfortunately, subsequently none of the investigators, including the authors of the present review, were unable to reproduce these results.

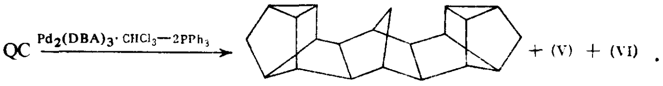
A more reliable method of synthesis of compound (XLI) consists apparently in the cyclocodimerisation of NBD with the *exo,trans,exo*-dimer (IV) in the presence of the $Ni(CO)_2 \cdot (PPh_3)_2$ catalyst.[10]

The saturated trimer (XLII) with two cyclopropane fragments has been obtained by the cyclotrimerisation of NBD with participation of the rhodium catalysts 5% Rh/C, $Rh(NBD)_2BF_4$, and $[Rh(CF_3CO_2)_2]_2$:[71,75,76]



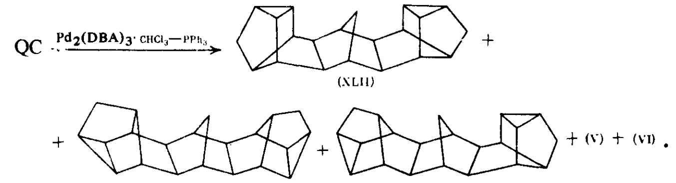
(XLII)

The synthesis of compound (XLII) under the influence of the dibenzylideneacetone (DBA) complex of palladium activated by triphenylphosphine has been reported recently:[9]

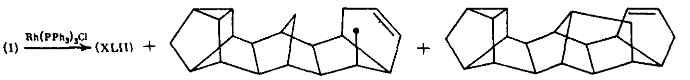


(XLII)

In a later publication[96] it was shown that Itoh's results required significant revision. It was found that the three isomeric cyclic trimers (XLII)–(XLIV) are formed together with the dimers (V) and (VI):

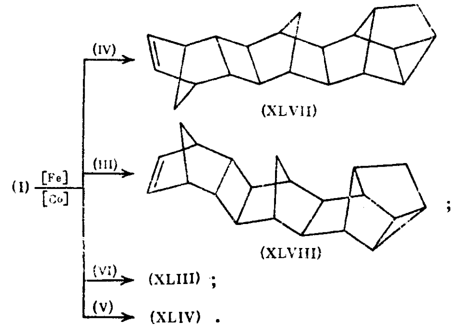


In addition, the trimer (XLII) was synthesised (in a low yield) by heating NBD with Wilkinson's complex $Rh(PPh_3)_3Cl$.[29,72] However, the preparative value of these studies is low, since the isolation of compound (XLII) in a pure form is very difficult owing to the presence in the reaction mass of the skeletal isomerisation products (XLV) and (XLVI):



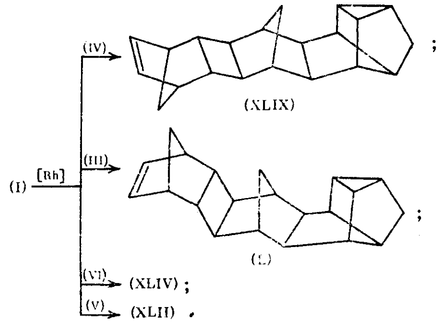
Effective methods have been developed[97] for the synthesis of the trimers (XLIII), (XLIV), (XLVII), and (XLVIII), which had not been described before, by the cyclodimerisation of NBD with the known dimers (III)–(VI) in the presence of the three-component catalytic systems $Fe(acac)_3$–$(Ph_2P$–$CH_2)_2$–Et_2AlCl and $Co(acac)_2$–$(Ph_2P$–$CH_2)_2$–Et_2AlCl. Three of the seven unsaturated NBD dimers, namely compounds (II) (X), and (XIV), whose molecules contain the norbornene fragment with *endo*-substituents, do not enter into the cyclodimerisation reaction with NBD.[97]

These results and also the regioselectivity of the addition of NBD to the "mixed" dimer (III), in which only the *exo*-disubstituted section of the molecule is involved, enabled the authors[97] to explain convincingly the inertness of the dimers (II), (X), and (XIV) by steric factors. It is noteworthy that the catalysts proposed in the above study make it possible to obtain one of the trimers (XLIII) by the direct cyclotrimerisation of NBD:[97,98]



Compounds (XLIII), (XLIV), (XLVII), and (XLVIII) have been formed as a result of the $[2_\pi + 2_\pi + 2_\pi]$-*exo,exo*-cycloaddition of the NBD molecule to the norbornene double bond of the corresponding dimer.

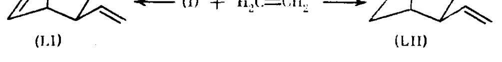
An interesting procedure for the synthesis of the NBD trimers by $[2_\pi + 2_\pi]$-*exo,endo*-cycloaddition has been proposed.[99] This reaction, which is accelerated by various rhodium complexes, namely $RhCl_3.4H_2O$, $Rh(acac)_3$, $[Rh(AcO)_2]_2$, etc., can serve as a convenient and promising method for the preparation of two previously unknown NBD trimers [(XLIX) and (L)] and two which were described previously[99] [(XLII) and (XLIV)].



V. THE CO-OLIGOMERISATION OF NORBORNADIENE WITH UNSATURATED COMPOUNDS

1. The Co-oligomerisation of Norbornadiene with Olefins

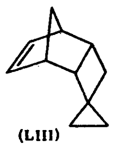
Olefins without electron-accepting substituents at the double bond are relatively inactive in cyclocodimerisation reactions with NBD. In particular, when ethylene reacts with NBD in the presence of zerovalent nickel complexes or the three-component cobalt catalyst $Co(acac)_2$–BPE–Et_2AlCl, the yields of 5-vinylnorbornene (LI) [100] and vinylnortricyclane (LII) [101–103] do not exceed 70%.

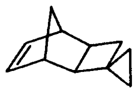


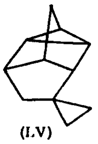
(LI) (LII)

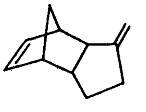
There are literature data indicating the possibility of the involvement of propene in the reaction with NBD,[102] but there are no experimental details in the above communication nor the physicochemical characteristics of the cyclic oligomers obtained.

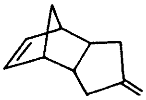
In contrast to the simplest olefins, methylenecyclopropane readily reacts with NBD to form $[2_\pi + 2_\pi]$-, $[2_\pi + 2_\pi + 2_\pi]$-, and $[2_\pi + 2_\sigma]$-codimers. The mode of cyclocodimerisation is determined mainly by the nature of the catalyst. For example, the complex Ni(COD)$_2$ promotes the formation of the $[2_\pi + 2_\pi]$codimers (LIII) and (LIV), the $[2_\pi + 2_\sigma]$codimer (LVI), and the $[2_\pi + 2_\pi + 2_\pi]$codimer (LV),[105] while palladium catalyst afford the $[2_\pi + 2_\sigma]$co-oligomers (LVII) and (LVIII).[106,107] The selectivity in the formation of the codimer (LIII) can be raised to 100% by introducing into the catalyst an equimolar amount of PPh$_3$.[105]

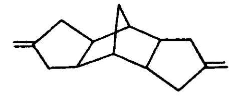

(LIII)


(LIV)


(LV)

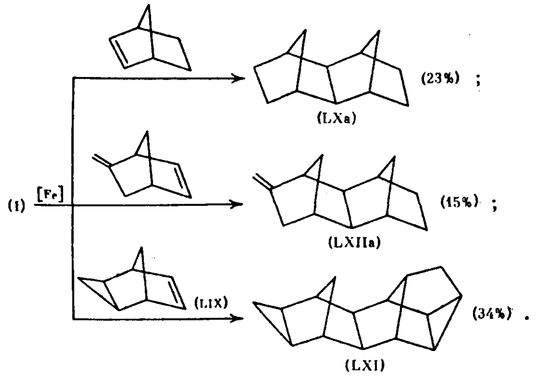

(LVI)


(LVII)


(LVIII)

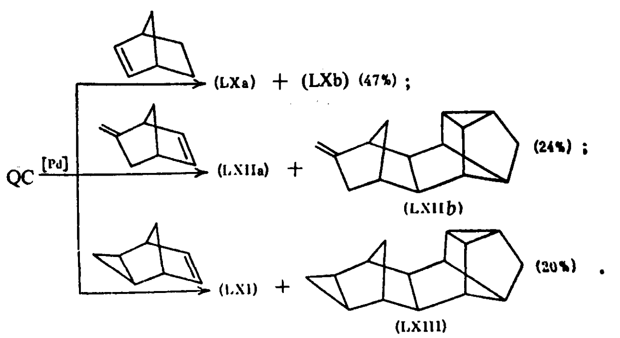
It was established subsequently[101,103,106,108] that cyclic olefins can also be involved in the reaction with NBD. A mixture of polycyclic hydrocarbons (yield ~22%) with a content of compound (VIa) of ~42%, was obtained from NBD and norbornene under the influence of the Co(acac)$_3$–BPE–Et$_2$AlCl catalyst.[101,103,106,108]

The codimerisation of NBD with norbornene, 5-methylenenorbornene and tricyclo$[3.2.1.0^{2,4}]$octa-6-ene (LIX) has been achieved using the Fe(acac)$_3$–BPE–Et$_2$AlCl catalytic system.[109]



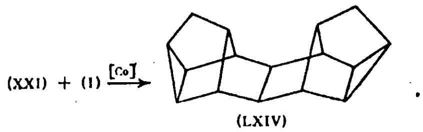
It is essential to note the high stereoselectivity in the activity of the catalytic system indicated. Only the *exo,exo*-codimers (LXa), (LXIIa), and (LXI) were obtained in all the experiments.

An alternative pathway to the synthesis of the hydrocarbons (LXa), (LXIIa), and (LXI) has been described.[96] A distinct characteristics of this method involves the use as the initial monomer not of BD but of its valence isomer—quadricyclane. The reaction is catalysed by the palladium complexes Pd$_2$(DBA)$_3$–CHCl$_3$ and Pd(acac)$_2$–PPh$_3$–AlEt$_3$.

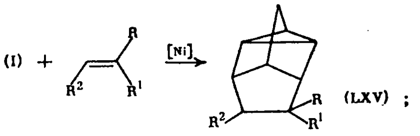


The scheme presented shows that the codimerisation of quadricyclane with cyclic olefins proceeds less selectively. Together with compounds (LXa), (LXIIa), and (LXI), the *exo,endo*-addition products (LXb), (LXIIb), and (LXIII) are present in the mixture. The ratio of the *exo,exo*- and *exo,endo*-isomers is approximately 2 : 3 and depends little on the structure of the cyclic olefins.

The cyclodimerisation of NBD with tetracyclo$[4.3.0.0^{2,4}.0^{3,7}]$non-8-ene has been achieved recently in the presence of the catalytic system Co(acac)$_2$–BPE–Et$_2$AlCl.[110] Under optimum conditions, the yield of the octacyclic compound (LXIV) is 53% relative to the NBD which has reacted:



The introduction of electron-accepting substituents tends to increase the reactivity of olefins in relation to codimerisation with NBD, the reaction proceeding strictly stereoselectively in accordance with the $[2_\pi + 2_\pi + 2_\pi]$addition mechanism with formation of substituted tetracyclo$[4.3.0.0^{2,4}.0^{3,7}]$nonanes (LXV):[8,111-114]

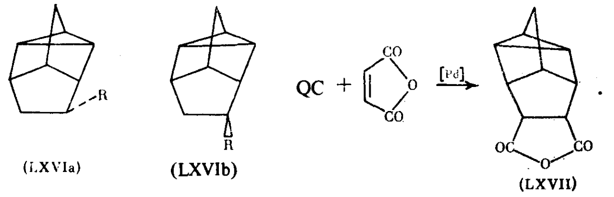


R = CN, CO$_2$Alk, COMe; R^1 = H, Me; R^2 = CO$_2$Me .

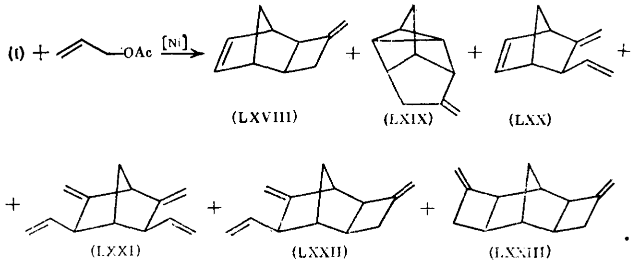
According to the literature,[11,111,119] such cyclodimerisation is catalysed by nickel complexes of different structure: Ni(CO)$_4$, Ni(CO)$_3$(PPh$_3$), Ni(CO)$_2$[P(OPh$_3$)]$_2$, Ni[P(OR)$_3$]$_4$ (R = alkyl or aryl), Ni(COD)$_2$, Ni(CH$_2$=CH–CN)$_2$, Ni(CN)$_2$.(PPh$_3$)$_2$, and Ni(acac)$_2$-PPh$_3$–Et$_2$AlCl. The systems based on bis(acrylonitrile)nickel and Ni(CN)$_2$(PPh$_3$)$_2$ are the most active: the codimerisation of acrylonitrile with NBD take place at 60–80 °C with yields up to 95%.[14,112] Analogous results have been obtained using the Co$_2$(CO)$_8$–PPh$_3$ system.[112]

In terms of their reactivity in codimerisation with NBD, olefins with electron-accepting substituents can be arranged in the sequence acrylonitrile > crotononitrile > methacrylonitrile > dimethyl maleate.[14,112] The ratio of the *exo*-isomer (LXIIIa) and the *endo*-isomer (LXIIIb) in these experiments is determined by the nature of the solvent and the structure of the organophosphorus activators—ligands,[110] and is almost independent of the size of the ester substituent in acrylates.[8] The use of quadricyclane in this reaction instead of NBD increases the yield of the codimer but does not affect the ratio of the *exo*- and *endo*-isomers.[8]

Under mild conditions, quadricyclanes react with maleic anhydride to form the codimer (LXVII) in the presence of the catalytic system $(DBA)_2Pd_2.CHCl_3$–PPh_3.[9]



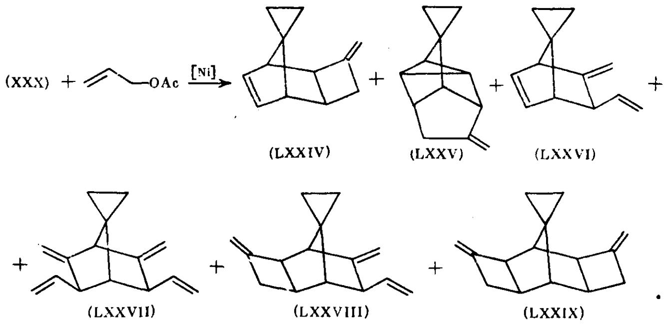
An unusual reaction pathway is observed in the co-oligomerisation of norbornadienes with allyl ethers under the influence of the three-component catalytic system $Ni(acac)_2$–$P(OR)_3$–$AlEt_3$:[120,121]



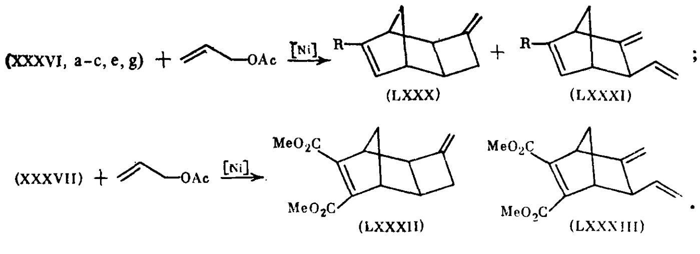
It follows from the above scheme that the reaction formally involves the addition to NBD of one or two allene molecules, but the process proceeds in a complex manner as can be seen from the structure of the products (LXX), (LXXI), and (LXXII).

The isomeric composition of the co-oligomers depends on temprature and the nature and structure of the organophosphorus ligand. At room temperature the main reaction products are the cyclic compounds (LXXVIII) and (LXIX). The most active catalysts have been obtained using alkyl phosphates as the promoting agents.

The co-oligomerisation catalysts are relatively insensitive to the structure of the substituents in the NBD molecule. For example, 7-spiro-cyclopropanenorbornadiene (XXX) reacts with alkyl acetate to form six isomers in an overall yield of ~80%.[120,121]



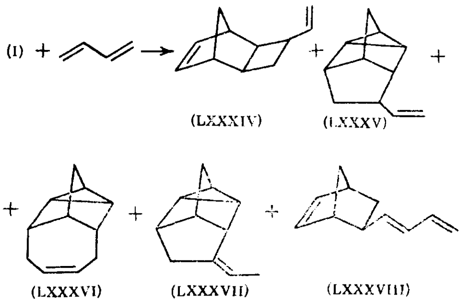
The composition of the reaction product simplifies when 2- and 2,3-substituted NBD are used.



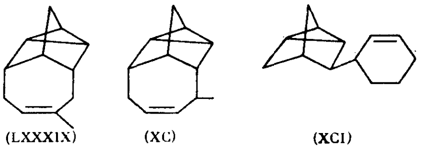
The reaction indicated is general and can serve as a promising method for the synthesis of polycyclic hydrocarbons containing the methylenecyclobutane group, which are otherwise difficult to obtain.[122]

2. The Co-oligomerisation of Norbornadiene with Dienes

The addition of dienes to NBD in the presence of metal complex catalysts based on nickel, iron, cobalt, and manganese compounds has been investigated in detail by Italian workers. Thus the codimerisation of butadiene and NBD results in the formation of a mixture of the polycyclic hydrocarbons (LXXXIV) and (LXXXV) in a high yield.[55,79,101,123,124]



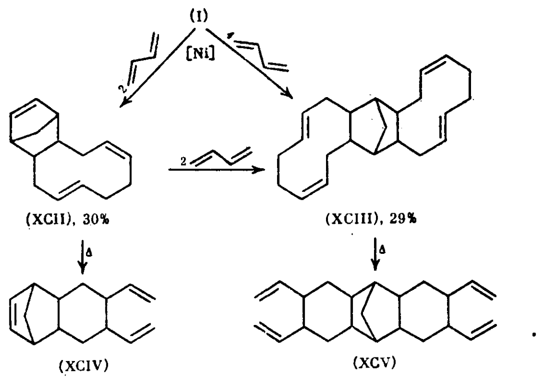
The codimer of 5-butadienylnorborn-2-ene (LXXXVIII) is obtained in a high yield and a selectivity up to 94% in the presence of the $Co(acac)_3$-1,2-bis(diphenylphosphino)ethane–$AlEt_3$ catalytic system.[79,125–127] The use of Et_2AlCl as the reductant tends to alter the direction of the reaction towards the formation of the codimer (LXXXVI).[101,128] The same three-component catalytic system has been used in the codimerisation of NBD with isoprene, piperylene, and cyclohexa-1,3-diene in order to obtain compounds (LXXXIX)–(XCI) respectively.[101,129–132]



According to Ref.133, tetracyclo[$5.4.0.0^{6,10}.0^{9,11}$]undec-3-ene (LXXXVI) can be obtained with a high selectivity from NBD in budadiene in the presence of iron complexes.

The best method of synthesis of compound (LXXXIV) (in a yield of 90%) consists in the [$2_\pi + 2_\pi$]cycloaddition of butadiene to NBD in the presence of the complex $(C_5H_5)Ti(CH_2Ph)_3$ at 135–155 °C.[134–136]

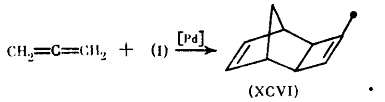
The mixed cyclo-oligomerisation of NBD and butadiene taken in molar proportions of 1 : 6 in the presence of the three-component system Ni(acac)$_2$–AlEt$_2$(OEt)–tris(*o*-biphenylyl) phosphite as the catalyst, results in the formation of compounds (XCII) and (XCIII), which isomerise at 150 °C to compounds (XCIV) and (XCV):[137]



(XCII), 30% (XCIII), 29%

(XCIV) (XCV)

The reaction of 1,2-dienes with NBD and its derivatives is extremely interesting. In the presence of zerovalent palladium complexes,[138,139] the unsubstituted allene reacts with NBD to form exclusively the $[2_\pi + 2_\pi]$cycloaddition product (XCVI):



(XCVI)

Under the influence of the three-component catalyst Co(acac)$_2$–PPh$_3$–Et$_3$AlCl, NBD and compound (XXX) react with allene via both $[2_\pi + 2_\pi]$ and $[2_\pi + 2_\pi + 2_\pi]$ mechanisms:[140]

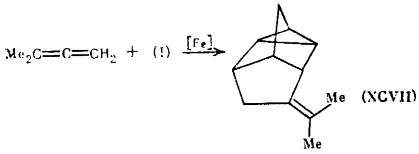
$$\text{(I)} + CH_2{=}C{=}CH_2 \xrightarrow{[Co]} \underset{85\%}{\text{(LXIX)}} + \underset{15\%}{\text{(LXXII)}} ;$$

$$\text{(XXX)} + CH_2{=}C{=}CH_2 \xrightarrow{[Co]} \underset{85\%}{\text{(LXXV)}} + \underset{19\%}{\text{(LXXIX)}} .$$

The main reaction product is a hydrocarbon with the deltacyclane structure, (LXIX) or (LXXV). The co-oligomers (LXXIII) and (LXXIX) are apparently formed in steps but the intermediate $[2_\pi + 2_\pi]$codimers were not detected in the reaction mixture.

A very complex composition of the products (up to 10 isomers) has been obtained in the co-oligomerisation of NBD with 1,1-dimethyl-, 1-cyclopropyl-, and 1-phenyl-allenes with cyclonona-1,2-diene. Their reactivity is inferior to that of allene, which is indicated by the high yield of the co-oligomers (~80%).[140]

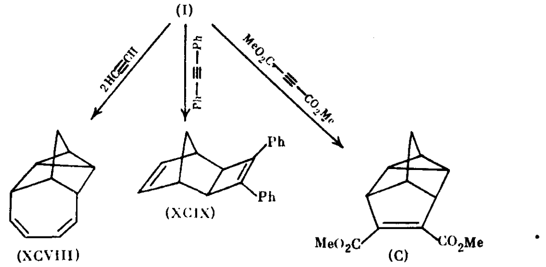
The catalyst obtained by reducing Fe(acac)$_3$ with diethylaluminium chloride directs the reaction of NBD with 1,1-dimethylallene towards the selective formation of the $[2_\pi + 2_\pi + 2_\pi]$codimer (XCVII):[55,123]



(XCVII)

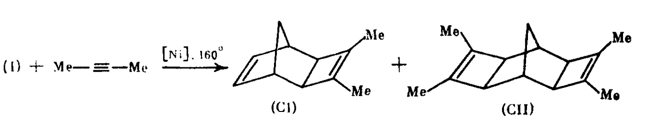
3. The Co-oligomerisation of Norbornadiene with Acetylenes

According to Schrauzer and Glockner,[112] the nickel complexes Ni(CO)$_2$(PPh$_3$)$_2$ and Ni(CN)$_2$(PPh$_3$)$_2$ catalyse the cycloaddition of acetylene, diphenylacetylene, and dimethyl acetylenedicarboxylate to NBD at 120 °C with formation of compounds (XCVIII), (XCIX), and (C):



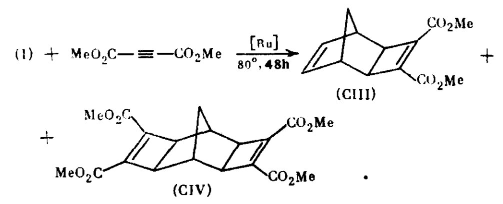
(XCVIII) (XCIX) (C)

The use of tetrakis[tri(2-ethylhexyl) phosphite]nickel increases the yield of compound (XCIX) to 74%.[141] In the presence of the same catalyst, but-2-yne reacts vigorously with NBD via the $[2_\pi + 2_\pi]$ mechanism, affording the tri- and tetra-cyclic hydrocarbons (CI) and (CII):



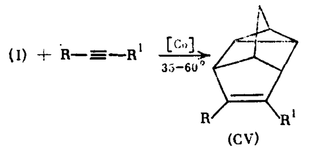
(CI) (CII)

NBD and dimethyl acetylenedicarboxylate interact via an analogous mechanism in the presence of the ruthenium complex [H$_2$Ru(PPh$_3$)$_4$], forming the *exo*-co-oligomers (CIII) and (CIV):[142]



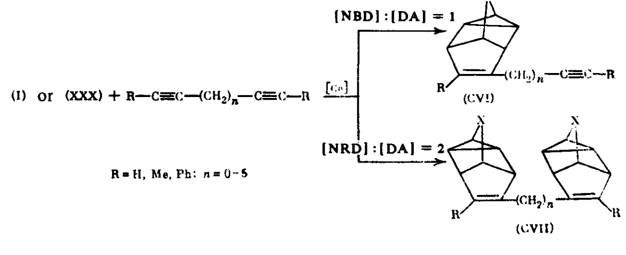
(CIII) (CIV)

Cobalt-containing systems, obtained by reducing Co(acac)$_2$ with Et$_2$AlCl in the presence of biphosphine, exhibit exceptionally high catalytic activity in the $[2_\pi + 2_\pi + 2_\pi]$cycloaddition of NBD to acetylene.[101,143–145] The highest yields of deltacyclene derivatives were obtained in experiments with acetylene and phenylacetylene.



(CV)

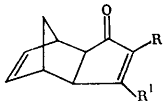
A novel pathway leading to the bisdeltacyclene structures (CVII), which are otherwise difficult to obtain, arises from the co-oligomerisation of NBD and compound (XXX) with diacetylenes (DA) under the influence of the Co(acac)$_2$–PPh$_3$–Et$_2$AlCl catalytic system:[140]



(CVI) (CVII)

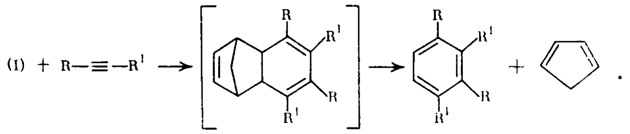
The yields of compounds (CVI) and (CVII) depend significantly on the distance between the acetylene fragments in DA and on the nature of the substituent, reaching 80% for $n \geq 3$ and R = H or Me. By altering the molar ratio of the monomers, the process can be directed towards the formation of the monoadduct (CVI) or the diadduct (CVII). In the reaction involving diphenyldiacetylene, the yield of compound (CVII) does not reach 10%, while 1,3-diacetylene fully polymerises under the reaction conditions.[140]

In the presence of the complexes $Co_2(CO)_8$ or $Fe(CO)_5$, the main products of the codimerisation of NBD with acetylenes are the cyclopentenone derivatives (CVIII).[146,147]



(CVIII)

The use of zerovalent iron and palladium complexes as catalysts of the cyclocodimerisation of NBD with acetylenes leads to the formation of 1,3-di- and 1,2,3,4-tetra-substituted benzenes (CX):[148,149]



(CIX) (CX)

Carbonaro et al.[148] and Suzuki et al.[149] postulated the intermediate formation of the thermodynamically unstable intermediate (CIX), which decomposes into cyclopentadiene and compound (CX).

Thus the co-oligomerisation of NBD with olefins, 1,2- and 1,3-dienes, and acetylenic hydrocarbons under the influence of nickel, palladium, cobalt, and iron complexes can serve as an effective method of the single-state synthesis of mono- and bis-tetracyclo[$4.3.0.0^{2,4}.0^{3,7}$]nonane (deltacyclane), tricyclo[$4.2.1.0^{2,5}$]nonane, and tetracyclo[$5.4.0.0^{6,10}.0^{9,11}$]undecane hydrocarbons.

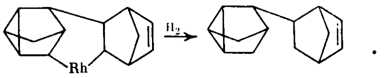
VI. THE MECHANISM OF THE DIMERISATION AND CODIMERISATION OF NORBORNADIENE

The cyclodimerisation and cyclocodimerisation of NBD and its derivatives belong to the so-called pericyclic reactions prohibited by symmetry rules. However, they are catalytically allowed although the causes of this fact have not so far been elucidated.[150–157]

In 1967 Mango and Schachtschneider[150] proposed a theory according to which the interaction of a transition metal atom with olefins entails a change in the symmetry of the highest occupied orbitals and the cyclisation reaction becomes allowed. There exists also another view on the role of the metal in catalysis according to which the role of the neutral catalyst atom consists in reducing the activation energy for the prohibited reaction and not in changing the symmetry of the orbitals in the reactants.[155]

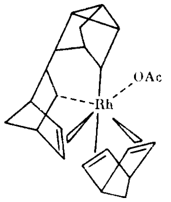
The experimental data accumulated permit the conclusion that the reactions indicated have a multistage mechanism. These include all the principal reactions of metal complex catalysis: coordination, oxidative addition, insertion, and reductive elimination.[9,154]

The key stage in the multistage mechanism of the cyclo-oligomerisation of olefins and dienes is the formation of metallocyclic compounds, which have been isolated and identified with the aid of modern physicochemical methods.[23,158–167] For example, the hydrogenation of a mixture of NBD and $(NBD)_2RhPF_6$ results in the formation of the hydrocarbon (CXII), for which one can postulate only one possible formation pathway—via the rhodacyclohexane organometallic compound (CXI):[162]

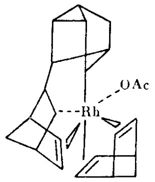


(CXI) (CXII)

The most reliable evidence for the multistage mechanism has been obtained in a study[7] of the isomerisation dimerisation of quadricyclane in the presence of rhodium catalysts. Organorhodium intermediate compounds (CXIII) and (CXIV), responsible for the formation of the molecules of NBD homo- and co-oligomers, have been observed and identified.



(CXIII)



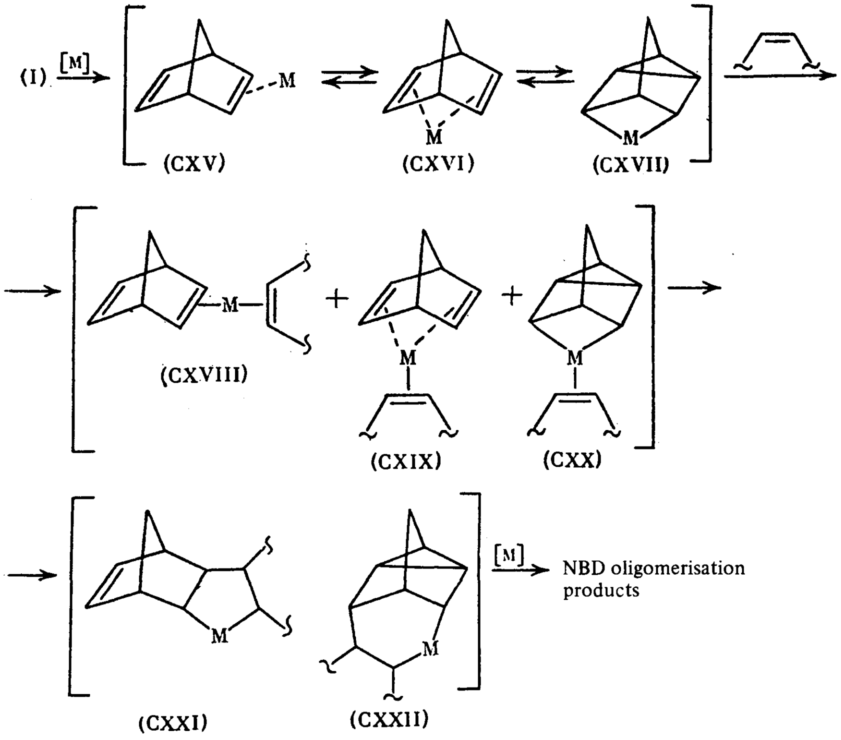
(CXIV)

Similar complexes were obtained in the reaction of hexafluorobutyne with NBD coordinated to rhodium via [$2_\pi + 2_\pi + 2_\pi$]cycloaddition. The structure of the rhodacyclobutane complex was determined by X-ray diffraction.[160] Analogous complexes are known for nickel, ruthenium, and iridium.[158,164,165]

Experimental results[75,88] show that the stereospecific [$4_\pi + 4_\pi$]dimerisation of NBD proceeds at a single centre, whose role is fulfilled by a singly-charged rhodium or cobalt complex.

At the present time there is no single view concerning the individual stages of the mechanism of the dimerisation, trimerisation, and codimerisation of NBD, which can be accounted for by the lack of direct and complete experimental evidence for the validity of a particular mechanism. Despite this, when account is taken of the literature data,[101,168,169] it is possible to postulate what is to some extent a general and universal mechanism of the cycloaddition of NBD involving [$2_\pi + 2_\pi$], [$2_\pi + 2_\pi + 2_\pi$], and [$4_\pi + 4_\pi$] steps on the basis of key catalytic reactions: oxidative addition, insertion, and reductive elimination.

According to this possible mechanism (see Figure), NBD is initially coordinated to the metal with formation of complexes of three types: (CXI)–(CXVII). The equilibrium position in this system is determined by the number of free coordination sites at the metal atom, the nature of the ligand environment, and the charge on the transition metal. It is known that NBD interacts with electrophilic species, forming preferentially compounds containing the nortricyclane system. Consequently, the equilibrium for complexes whose central metal atom has a positive charge is displaced towards the formation of compound (CXVII) and, the greater the charge on the atom, the greater the shift of the equilibrium to the right. Successive coordination of the olefin leads to the intermediates (CXVIII)–(CXX), whose intramolecular reactions proceed either via the synchronous formation of metal—carbon and carbon—carbon σ-bonds or via the insertion of the olefin into the metal—carbon bond with formation of the metallocyclic compounds (CXXI) and (CXXII). The subsequent key stage in the NBD dimerisation and codimerisation reactions is the reductive elimination of the transition metal atom, which can again initiate a new catalytic cycle.



The possible mechanism of the dimerisation and codimerisation of norbornadiene.

The stereochemistry of the isomers formed should be fully determined by the charge on the central metal atom, its coordination number, and its ligand environment.

For the final elucidation of the mechanism of the NBD cycloaddition reaction, it is essential to carry out kinetic studies, to isolate the intermediates, and to investigate their properties in the greatest possible detail.

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During the preparation of the manuscript for the press, new communications and studies on the homo- and co-dimerisation of NBD and its derivatives in the presence of transition metal complexes were published.[170–173] The results of investigations of the codimerisation of NBD with cycloheptatriene under the influence of titanium-containing catalysts, with formation of new types of penta- and hexa-cyclic polycyclic compounds,[170] are of greatest interest. Several studies have been devoted to the cyclodimerisation of NBD and of its 7-substituted derivatives via the $[4_\pi + 4_\pi]$cycloaddition mechanism.[171–173]

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Pseudoazulenes as π-Isoelectronic Analogues of Azulene

Yu.N.Porshnev, V.A.Churkina, and M.I.Cherkashin

The principal methods of synthesis and the chemical and physicochemical properties of pseudoazulene are described. Attention is concentrated on the latest studies which have not been taken into account in the published reviews. Certain aspects of the uses of pseudoazulene compounds are examined.

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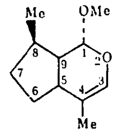
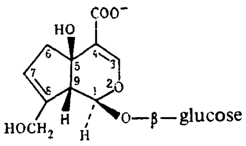
I. INTRODUCTION

Only individual terpenoid representatives of hydrogenated pseudoazulenes of the cyclopentapyran series, such as 1-methoxymyodesert-3-ene (I) which forms part of the structure of *Myoporum deserti* (Myoporaceae) as the iridoid constituent and has been found in plants growing in the moist regions of Australia, have been discovered in nature.[1] The iridoid—the glycoside (II)—present in *Lanthana camara* (Verbenaceae) and detected in 150 plant species in Africa and tropical America, has been identified:

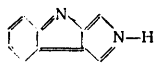


(I)

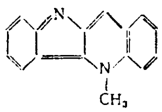


(II)

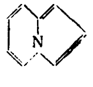
Individual pseudoazulene systems are components in the structures of alkaloids. Thus the alkaloids sempervirine and alstonine contain the 2*H*-pyrido[3,4-*b*]indole (III) system,[3–7] while the alkaloid cryptolepine has the structure (IV).[8] The hydrogenated indolizine system (V) is present in the molecules of strychnine, securinine, and the Veratrum alkaloids germine, cevine, and protoverine. The 1- and 3-alkylpurines (VI) and (VII) are used as model substances which participate in glycosylation reactions and whose reactivity is equal to that of antibiotics and nucleic acids.[9,10]



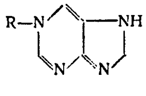
(III)



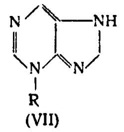
(IV)



(V)



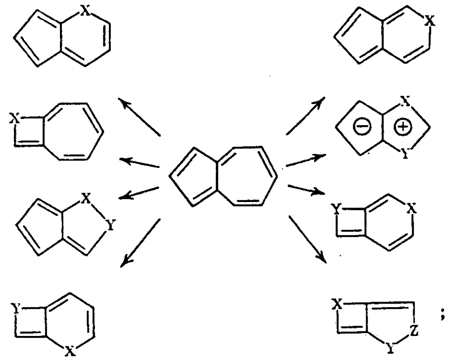
(VI)



(VII)

The advances in quantum chemistry regarding the creation of the theory of aromaticity have promoted an intense development during the last three decades of the chemistry of heterocarbonium aromatic systems, among which analogues of the non-benzenoid aromatic azulene system, namely pseudoazulenes, are of special interest. Formally, they can be obtained by replacing a two-electron carbon–carbon double bond in the aromatic system by the unshared electron pair of the heteroatom, whereupon the aromatic character of the system is usually retained.[11–13] This principle of structural analogy, which has been known for a long time in the benzene–thiophen–furan–pyrrole series, was first applied in 1957 by Boyd[14] and Mayer[15] and later also by other workers[16,17] to a large group of heterocyclic compounds—pseudoazulenes, which are π-isoelectronic analogues of azulene. The chemistry of these systems has only just begun to develop despite the fact that the fundamental studies by Robinson and co-workers[11–13] were published in the first quarter of this century.

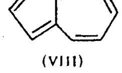
According to the above principle, numerous representatives of pseudoazulene systems in which one, two, or three double bonds have been replaced by heteroatoms can be formally obtained from azulene:



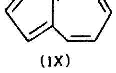
X, Y, Z = –O–, –S–, –NR–, –Se–, –Te–.

For the azazulenes (VIII) and (IX), polyazazulenes, and heteroniaazulenes, the analogous "reactions" are also possible.[18,19]

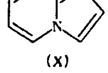
The number of possible systems increases greatly when different heteroatoms are used simultaneously. Dinuclear condensed heterocyclic systems with a nitrogen atom common to both rings, namely quinolizines, are also regarded as the pseudoazulenes (V) and (X).



(VIII)

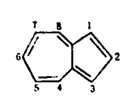
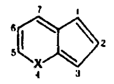
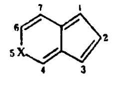
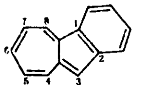
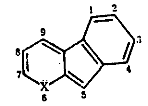
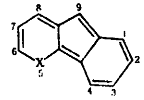
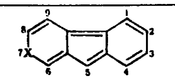
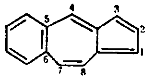
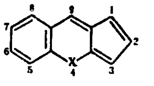
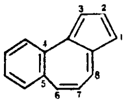
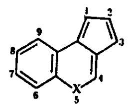
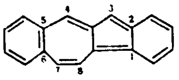
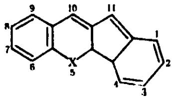
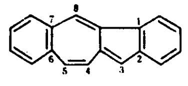
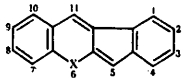
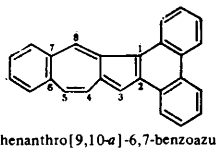
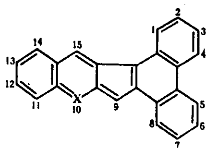


(IX)



(X)

Table 1. Pseudoazulenes with one heteroatom in the six-membered ring.

Azulene	Pseudoazulene	Code	X	Name		Refs.
				in IUPAC nomenclature	trivial	
10 π-Electron systems						
 azulene		(XI)	NR	1H-pyrindine	azalene	[12, 13, 51, 60, 73]
		(XII)	O	cyclopenta[b]pyran	oxalene	[14, 51, 53, 102]
		(XIII)	S	cyclopenta[b]thiapyran	thialene	[15, 18, 34, 35, 106]
		(XIV)	NR	2H-pyrindine	isoazalene	[36, 37, 62, 72, 110]
		(XV)	O	cyclopenta[c]pyran	iso-oxalene	[62]
		(XVI)	S	cyclopenta[c]thiapyran	isothialene	[34—37, 61—64]
14 π-Electron systems						
 1,2-Benzoazulene		(XVII)	NR	6H-indeno[2,1-*b*]pyridine	1,2-benzoazalene	[101]
		(XVIII)	O	indeno[2,1-*b*]pyran	1,2-benzoxalene	[104]
		(XIX)	S	indeno[2,1-*b*]thiapyran	1,2-benzothialene	[34]
		(XX)	NR	5H-indeno[1,2-*b*]pyridine	2,3-benzoazalene	[59]
		(XXI)	S	indeno[1,2-*b*]thiapyran	2,3-benzothialene	[55]
		(XXII)	NR	7H-indeno[2,1-*c*]pyridine	1,2-benzoisoazalene	[66—68, 116
 5,6-Benzoazulene		(XXIII)	NR	4H-cyclopenta[*b*]quinoline	5,6-benzoazalene	[16, 19, 43—46]
		(XXIV)	O	cyclopenta[*b*]chromene	5,6-benzoxalene	[14, 16, 25, 57]
		(XXV)	S	cyclopenta[*b*]thiachromene	5,6-benzothialene	[25, 28, 38]
 4,5-Benzoazulene		(XXVI)	NR	5H-cyclopenta[*c*]quinoline	7-benzoisoazalene	[29]
18 π-Electron systems						
 1,2; 5,6-Dibenzoazulene*		(XXVII)	NR	5H-indeno[1,2-*b*]quinoline	2,3; 5,6-dibenzoazalene	[12, 13, 27]
 1,2; 6,7-Dibenzoazulene		(XXVIII)	NR	6H-indeno[2,1-*b*]quinoline	1,2; 5,6-dibenzoazalene	[28, 52, 74, 103]
		(XXIX)	O	indeno[2,1-*b*]chromene	1,2; 5,6-dibenzoxalene	[14, 26, 28, 57, 74, 77, 80, 103—105]
		(XXX)	S	indeno[2,1-*b*]thiachromene	1,2; 5,6-dibenzothialene	[34, 49, 111]
Systems containing more than 18 π-electrons						
 Phenanthro[9,10-*a*]-6,7-benzoazulene*		(XXXI)	NR	10H-dibenzo[4,5; 6,7]-indeno[2,1-*b*]quinoline	phenanthro[9,10-*a*]-5,6-benzoazalene	[24]

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*Azulene systems having this structure are unknown.

They constitute a large independent group of pseudoazulenes, whose chemistry has been described in a monograph.[20] A review has been devoted to the chemistry of the indolizines (V).[21] Almost all the pseudoazulene systems known at the present time are represented in the review of Timpe and El'cov.[22]

The number of existing nitrogen-containing pseudoazulenes is much greater than that of the sulphur- and oxygen-containing compounds; only one pseudoazulene system containing selenium as the heteroatom is known.[23] Systems containing tellurium as well as systems with a four-membered ring are so far unknown, which can be explained by the instability of these products in the former case or the considerable angular ring strain in the latter. The influence of the heteroatom on the electronic structure, the electronic spectra, the stability, and the reactivity has been most fully investigated for pseudoazulene systems in which the unshared electron pair of the heteroatom replaces one double bond in the seven-membered ring of azulene or benzoazulenes. For this reason, we shall confine ourselves to the consideration of the systems presented in Table 1.

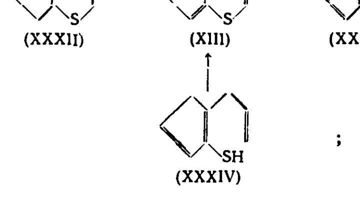
The [*b*]-series pseudoazulenes (XI)–(XIII) and the [*c*]-series pseudoazulenes (XIV) and (XVI) are non-alternant 10π-isoelectronic analogues of azulene. Compounds (XVII) to (XXVI) are isoanalogues of the 14π-electron systems of 1,2-, 5,6-, and 4,5-benzoazulenes. For the 18π-electron systems (XXVII) and (XXX), azulenes with an analogous structure are so far unknown and this is also true of the new pseudoazulene system (XXXI) obtained in 1975.[24] It was initially suggested that pseudoazulenes containing a sulphur atom, an oxygen atom, or an NR group be designated as thialenes,[15] oxalenes,[25] and azalenes[17] respectively. This nomenclature, based on the type of heteroatom, is not always used although it effectively explains the genetic relation with azulene. Specific compounds are usually named in accordance with IUPAC rules, the pyrindines (XI) and (XIV) constituting an exception. The compounds listed in Table 1 are arranged in such a way that the cyclopentane ring is placed on the right-hand side of the main pseudoazulene system, while the heteroatom on the left-hand side is placed in the lower half of the heterocycle. The first carbon atom is located in the upper angle of the cyclopentane component of the main system. The remaining atoms are numbered clockwise, the heteroatom being numbered in accordance with the general sequence. The above nomenclature is most widely used and has already been adopted in a series of well known publications.[14,26–29]

II. METHODS OF SYNTHESIS OF PSEUDOAZULENES

The methods of synthesis of pseudoazulenes differ significantly from those for azulenes, since its molecular skeleton is obtained in different ways, depending on the required pseudoazulene system. The methods of synthesis can be combined, for example, in accordance with the type of the last stage leading to pseudoazulenes. A common stage of this kind in the syntheses of both pseudoazulenes and azulenes is the dehydration of saturated compounds.

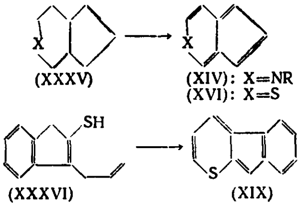
1. Dehydrogenation of Saturated Precursors of Pseudoazulenes

Historically the first and for a long time the only method of synthesis of azulene hydrocarbons was dehydrogenation of bicyclic precursors with the bicyclo[5.3.0]decane structure or the corresponding partly saturated compounds.[30–33] The dehydrogenation of more or less hydrogenated compounds, already having the heterocyclic skeleton of pseudoazulenes, is used only for sufficiently stable compounds. Numerous thialenes, of both [*b*]- and [*c*]-series, namely compounds (XIII), (XVI), and (XIX), have been obtained in this way.



(XXXII) (XIII) (XXXIII)

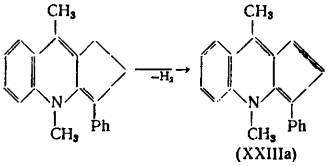
(XXXIV) ;



(XXXV) (XIV): X=NR (XVI): X=S

(XXXVI) (XIX) .

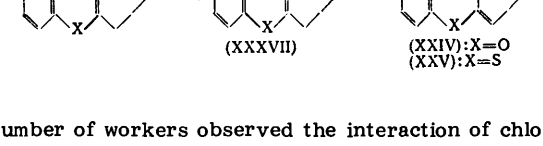
Hydrogenated sulphur-containing heterocycles, for example, compounds (XXXII), (XXXIII), and (XXXV), or the open-chain mercaptans (XXXIV) and (XXXVI),[34] are dehydrogenated in the gas phase over Pd/C at 300–350 °C.[35–38] The overall yield depends on the dehydrogenation stage, which frequently proceeds with a high (~30%) yield; it can also amount to only a few per cent owing to the low activity of the catalyst.[37] However, this method is still the best procedure for the synthesis of not only thialenes but also 2-phenylpyrindine (XIV).[36] Other pseudoazulene systems, for example, substituted 4*H*-cyclopenta[*b*]quinoline (XXIIIa), can also be conveniently obtained in this way,[17] but the dehydrogenation is carried out in boiling xylene for 10 h in an atmosphere of nitrogen with the same catalyst and the yield is 53%.



(XXIIIa) .

On dehydrogenation over Pd/C and also when the Cu_2Cl_2/C catalysts are used at 300 °C or sulphide is used at 300 °C, oxygen-containing precursors [for example, compound (XXXIII, X = O)] give rise to only tarry products.[37]

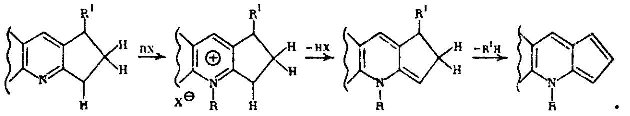
Azulene precursors are dehydrogenated under very mild conditions by chloranil and for this reason, the latter is widely used in the synthesis of azulenes containing substituents unstable at high temperatures.[39–42] For effective dehydrogenation, it is essential that the precursor should already possess a high degree of unsaturation. Chloranil has been used extremely rarely for the synthesis of pseudoazulenes.[25,35] The synthesis of the unsubstituted pseudoazulenes (XXIV) and (XXV) from chromone and thiachromone respectively using the dehydrogenation of compound (XXXVII, X = O or S) by chloranil has been described,[25] but the author did not indicate the dehydrogenation conditions and the reaction products were not isolated in a pure form:



(XXXVII) (XXIV):X=O (XXV):X=S .

A number of workers observed the interaction of chloranil with pseudoazulenes, for example, with 4*H*-cyclopenta[*b*]quinoline (XXIII) and 5*H*-cyclopenta[*c*]quinoline (XXVI), the latter being substituted by the chloranil residue in the 1- and 3-positions.[29,43,44]

Dehydro-compounds of the type of (XXXVIII) can be converted into fully aromatic systems by the multistage elimination of hydrogen atoms in the saturated cyclopentane or cyclopentene rings, or by the dehydrohalogenation of quaternary salts, or by some other elimination reaction:

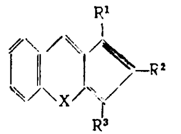


(XXXVIII) (XXXIX) (XL)

The acid-catalysed elimination of water from the hydroxy-derivative (XL, R^1 = OH) proceeds especially effectively.[45,46] It is then essential to maintain appropriate conditions exactly, since pseudoazulenes can be decomposed by acid. An instance of photochemical dehydrogenation is known.[24]

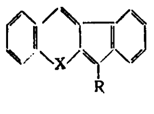
2. Condensation of Aromatic Aldehydes and Ketones

The method considered above is a general procedure for the conversion of compounds already containing the pseudoazulene skeleton into pseudoazulenes proper. Since new C–C and C–X bonds can arise in condensation reactions, it is always possible to select suitable initial compounds which give rise to the pseudoazulene system; dehydrogenation is then altogether unnecessary. The form of the initial compounds can be specified by the required structure of the final product. For example, the condensation of salicylaldehyde or *o*-mercaptobenzaldehyde with aryl-substituted Δ^2-cyclopentenones in the presence of piperidinium acetate in benzene yielded the arylsubstituted benzo[*b*]cyclopenta[*e*]pyrans {or cyclopenta[*b*]chromenes} (XXIVa–c)[14,27,47] and the corresponding thiapyrans {or cyclopenta[*b*]thiachromenes} (XXV*a*):[28]



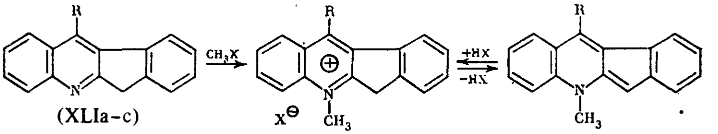
(XXIV a–c): X = O
(XXVa): X=S
a: R^1=R^3=H; R^2=Ph [14, 47]
b: R^1=R^2=Ph; R^3=H [27]
c: R^1=H; R^2=R^3=Ph [28] .

This method is particularly convenient for the synthesis of tetracyclic pseudoazulenes which are sometimes formed in a yield up to 80%. Indeno[2,1-*b*]chromene (XXIXa) and indeno[2,1-*b*] thiachromenes (XXX, R = H) have been obtained by condensing 2-indanone with salicylaldehyde and *o*-mercaptobenzaldehyde respectively.[28,48,49] The condensation of substituted 2-indanones or 2-indanoneimines with salicylaldehyde leads to 5-substituted derivatives of indeno[2,1-*b*]chromene



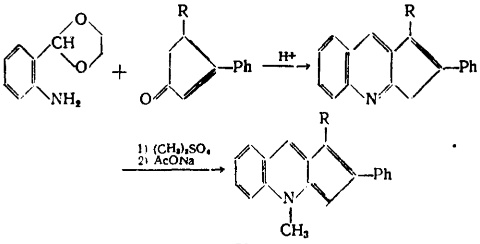
(XXIX a–e): X=O
(XXX): X=S [28.49]
a: R = H (Refs.14,48)
b: R = CH_3 (Ref.50)
c: R = 2-indanyl (Ref.50)
d: R = $COOC_2H_5$ (Ref.50)
e: R = CN (Ref.28) .

However, nitrogen-containing pseudoazulenes cannot be obtained in this way; the attempts to carry out the condensation in a neutral or alkaline medium (alkali in alcohol or piperidine in benzene) do not yield the final products directly. The reaction of the ethylene acetal of *o*-aminobenzaldehyde with phenyl-Δ^2-cyclopentenones does not afford pseudoazulenes under these conditions and it does not even give rise to Claisen condensation products.[51] The condensation of 2-indanone with *o*-aminobenzaldehyde, *o*-aminoacetophenone, or *o*-aminobenzophenone in an acid medium results in the formation of compounds (XLIa–c), dehydrogenated to the optimum extent, which are converted by quaternisation and subsequent alkaline cleavage of the quaternary salts into nitrogen-containing pseudoazulenes (XXVIIIa–c) in approximately 25% yield:[52]



(XLIa–c)
a: R = H
b: R = CH_3
c: R = Ph
(XXVIIIa–c)

Since *o*-aminobenzaldehyde is unstable, it is possible to use its ethylene acetal, whose condensation with 3-phenyl- and 3,4-diphenyl-Δ^2cyclopentenones in alcoholic solution of hydrochloric acid leads to the pseudoazulenes (XXIIIb, c) in good yield (up to 80%):[51,53]

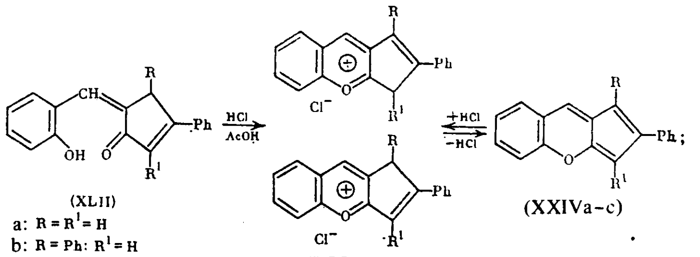


(XXIIIb, c)

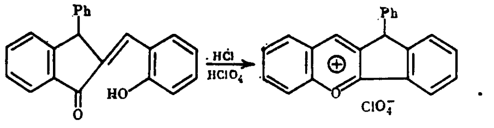
3. Deprotonation of Pyridinium, Quinolinium, Pyrylium, and Thiapyrylium Salts

The deprotonation of heteronium salts as a method of synthesis of pseudoazulene systems is logically a continuation of the previous subsection and is closely related to it in the synthetic sense, because the majority of the intermediates and salts based on them are obtained in this instance by condensing aldehydes and aromatic (and also α,β-unsaturated) ketones. The deprotonation of heteronium salts actually constitutes the dehydrogenation stage, which completes the synthesis of the pseudoazulene, but, since the number of final systems obtained in this way is fairly large and the reaction itself does not proceed smoothly with all salts, we shall consider this stage in a separate Section.

Salicylaldehyde undergoes the Claisen condensation with phenyl-substituted Δ^2-cyclopentenones of 1-indanone in alkaline media with formation of the corresponding hydroxychalcones (XLII) or (XLIII),[54,55] which afford the benzopyrylium salts (XLIVa–c) and (XLV) in a mixture of acetic and hydrochloric acids. However, whereas a solution of the salts (XLIVa–c) gives rise to the pseudoazulenes (XXIVa–c) on dilution with water, compound (XLV) decomposes on hydrolysis in the presence of sodium acetate:[55–57]

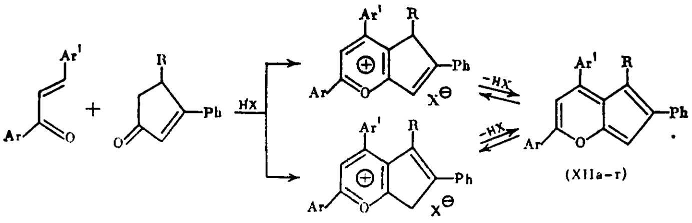


(XLII)
a: R = R¹ = H
b: R = Ph: R¹ = H
c: R = H; R¹ = Ph
(XLIVa–c)
(XXIVa–c) .



(XLIII) (XLV)

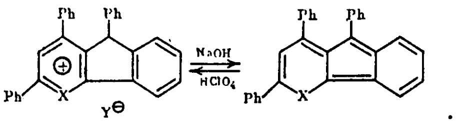
Chalcones and derivatives of phenyl-substituted Δ^2-cyclopentenones condense on treatment with $FeCl_3$ in acetic anhydride into the chloroferrates (XLVIa–d) in 35% yield. On treatment with sodium acetate, both the chloroferrates and perchlorates (XLIVa–d) give rise to cyclopenta[*b*]pyrans (XXIIa–d) in high yields (up to 90%):[47,58,59]



(XLVIa–r) (XIIa–r)

a: R = H, Ar = Ar' = Ph; b: R = Ar = Ar' = Ph; c: R = Ph, Ar = *n*-$CH_3OC_6H_4$, Ar' = Ph; d: R = Ph, Ar = Ph, Ar' = *p*-$CH_3OC_6H_4$; $X^- = FeCl_4^-$, ClO_4^-.

The tetrachloroferrate (XLVI) has been obtained analogously by the reaction of benzylidenacetophenone with 3-phenyl-1-indanone (XLVII) (yield 48%) and was converted into the perchlorate (XLVIII) by treatment with 70% perchloric acid. The condensation of equimolar amounts of acetophenone with 2-benzylidene-3-phenyl-1-indanone gives rise to the chloroferrate (XLVII) in only 20% yield:[55]

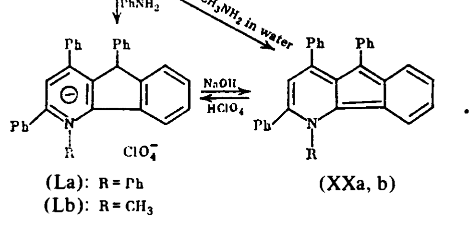


(XLVII): X = O, Y = $FeCl_4$
(XLVIII): X = O, Y = ClO_4
(XLIX): X = S, Y = ClO_4

(XXIa): X = S

On treatment with a 10% aqueous solution of Na_2S and subsequent addition of 20% perchloric acid, the perchlorate (XLVIII) gives rise to the thiapyrylium salt (XLIX) (yield 93%), which is deprotonated with an aqueous alcoholic solution of alkali and sodium acetate to form 2,4,5-triphenylindeno[1,2-*b*]thiapyran (XXIa). Hot water also hydrolyses the salt (XLIX) but more slowly.

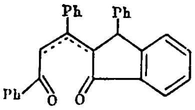
On interaction with aniline, the perchlorate (XLVIII) is converted into the *N*-phenylpyridinium salt (La) in 59% yield. The deprotonation of the salt with aqueous-alcoholic alkali affords 1,2,4,5-tetraphenyl-1*H*-indeno[1,2-*b*]pyridine (XXa). Treatment of the same perchlorate (XLVIII) with 30% aqueous methylamine leads to a 55% yield of 1-methyl-2,4,5-triphenyl-1*H*-indeno[1,2-*b*]pyridine (XXb), which can be converted into the substituted *N*-methylpyridinium perchlorate (Lb):



(La): R = Ph
(Lb): R = CH_3

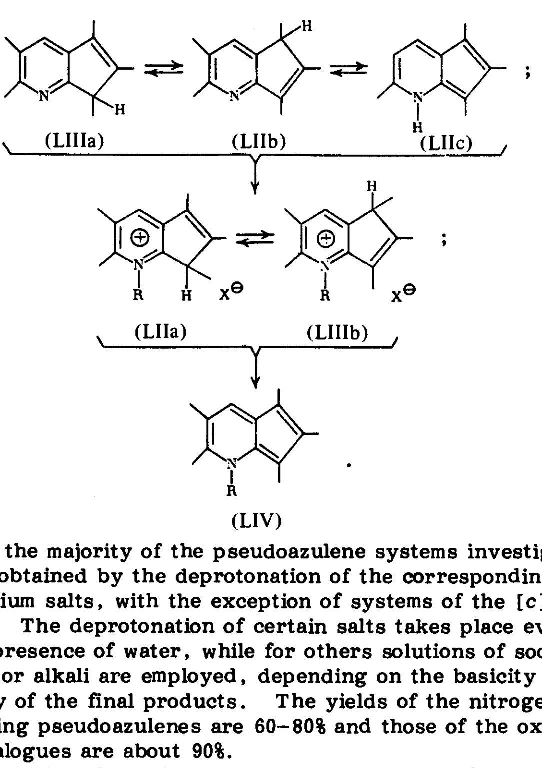
(XXa, b)

Whereas the heteronium salts of phenyl-substituted derivatives of cyclopenta[*b*]chromene (XLIV), cyclopenta[*b*]pyran (XLVI), indeno[1,2-*b*]thiapyran (XLIX), and indeno[1,2-*b*]pyridine (L) produce the corresponding pseudoazulenes on hydrolysis with aqueous-alcoholic solutions of alkali or sodium acetate, indeno [1,2-*b*]chromylium perchlorate (XLV) and indeno[1,2-*b*]pyrylium perchlorate (XLVIII) only regenerate the initial compounds under the same conditions, i.e. 3-phenyl-2-salicylidene-1-indanone (XLIII) and 2-(3-oxo-1,3-diphenylpropylidene)-3-phenyl-1-indanone (LI) respectively.



(LI)

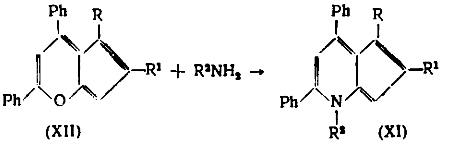
The quaternary salts of nitrogen-containing pseudoazulenes are obtained by the quaternisation of the corresponding heterocyclic bases with alkyl halides or tosylates in aprotic solvents.[28,45,51–53,60] Despite the tautomerism of the base (LII) [the isomers (LIIa–c) are possible], alkylation results in a good yield of the quaternary salts (LIII) (the *C*-alkylation products were detected only in trace amounts). Alkaline deprotonation of the quaternary salts (LIII) leads to the pseudoazulenes (LIV):



(LIV)

Thus the majority of the pseudoazulene systems investigated can be obtained by the deprotonation of the corresponding heteronium salts, with the exception of systems of the [*c*]-series. The deprotonation of certain salts takes place even in the presence of water, while for others solutions of sodium acetate or alkali are employed, depending on the basicity and stability of the final products. The yields of the nitrogen-containing pseudoazulenes are 60–80% and those of the oxygen-analogues are about 90%.

The reactions involving the direct substitution of the heteroatoms in the pseudoazulene systems must also be considered, since they permit the direct transition from, for example, oxalenes to pyrindines:[51,53,55,61,62]



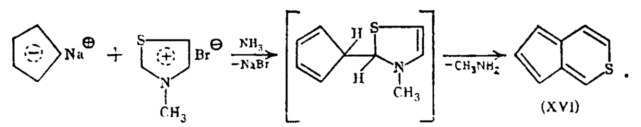
(XII) (XI)

After brief heating of compound (XII) with an excess of aniline, benzylamine, or butylamine in dimethylformamide (DMF), 1-substituted-1*H*-pyrindines (XI) were obtained in good yields.[51–53] If pyrylium perchlorates corresponding to the pyrans (XII) are introduced into the reaction, then the pyrans (XII) are formed as intermediates under the reaction conditions. A decisive factor for the successful occurrence of the reaction is evidently the high boiling point of DMF since, on heating to the boiling point in 10% alcoholic solution of ammonia,[47,58] and also on heating in ethanol with amines, compounds (XII) remain unchanged. Oxalenes, having an oxygen atom linked directly to the aromatic ring, cannot be converted in this way into nitrogen-containing pseudoazulenes. The attempts to convert 5,6-benzoxalene (XXIV) into 4*H*-cyclopenta[*b*]quinoline (XXIII) were unsuccessful (only polymeric products of the condensation of the initial compound were obtained[51,55]).

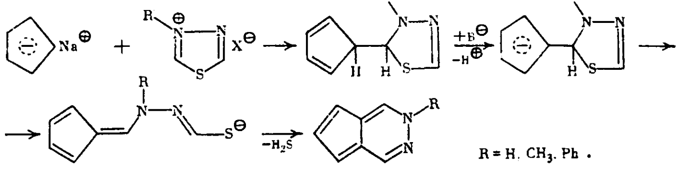
4. Other Methods of Synthesis

Apart from those described above, there exist several more methods of synthesis of pseudoazulenes. Although these are not quite so common, they can be used successfully in certain cases.

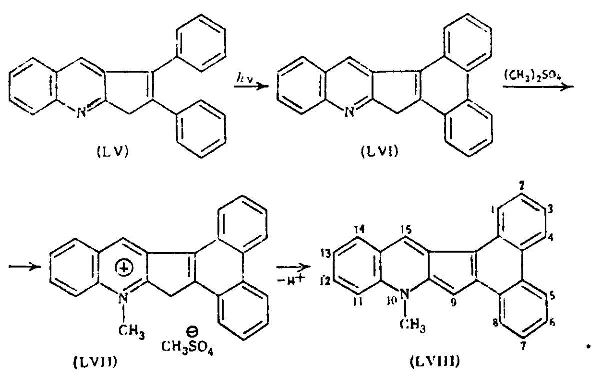
Analogously to the synthesis of the azulene by the Hafner method, the cyclopentadienyl anion can be used to obtain cyclopenta[*c*]thiapyran:[63,64]



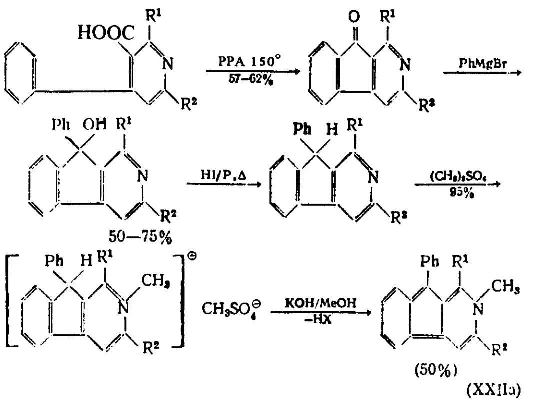
The yield of compound (XVI) is only 10%, but this method actually consists of only a single stage. So far, it has been the only procedure for the synthesis of 2*H*-cyclopenta[*d*]pyridazine:[65]



The photochemical oxidative cyclisation of 1,2-diphenyl-3*H*-cyclopenta[*b*]quinoline (LV) leads to the formation of a new hexacyclic structure (LVI).[24] Subsequent quaternisation with dimethyl sulphate and treatment with sodium acetate afford the fully conjugated polycyclic system (LVIII)—10-methyldibenzo[4,5,6,7]indeno[2,1-*b*]quinoline in 54% yield:

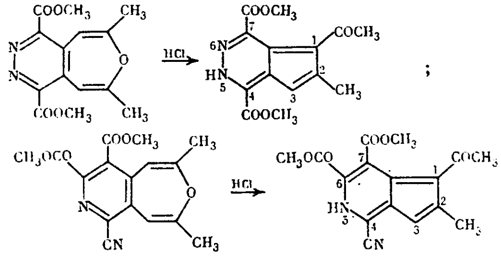


The synthesis of the 2*H*-indeno[2,1-*c*]pyridine derivative (XXIIa) has been described:[66–68]



PPA = polyphosphoric acid.

On treatment with HCl, oxepinopyridazine and oxepinopyridine derivatives are capable of rearranging to the corresponding pseudoazulenes—5*H*-cyclopenta[*d*]pyridazine and 5*H*-cyclopenta[*c*]pyridine:[69]



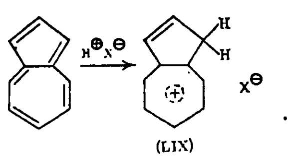
III. CHEMICAL PROPERTIES

The reactivity of pseudoazulenes has so far been inadequately investigated and information concerning the behaviour of many systems in chemical reactions is totally lacking. Data conerning the preferred reaction centres, obtained as a result of quantum-chemical calculations, are examined below. The examples of reactivity known at present are in the main consistent with these theoretical data and indicate a rigorous analogy with the properties of azulene. The enhanced electron density in the five-membered ring and the electron deficiency of the atoms of the heterocycle are responsible for the high reactivity of the former and the passivity of the latter with respect to electrophiles. Like azulene, pseudoazulenes readily form π-complexes with various π-acids: trinitrobenzene, picric acid, etc.

The trinitrobenzene complexes are frequently used for the purification, identification, and isolation of unstable pseudoazulenes, since such complexes readily decompose into their components during chromatography on alumina. Trinitrobenzenates are sometimes introduced into electrophilic substitution reactions,[70] the insoluble trinitrobenzene being subsequently readily removed.

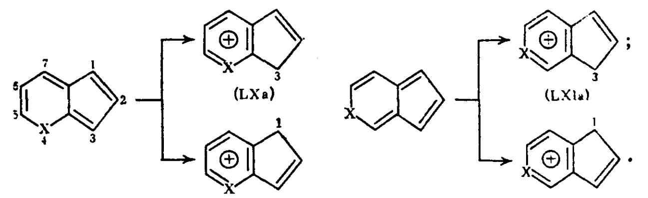
1. Basicity

The high basicity of azulene is responsible for the formation of the azulenium salt (LIX) on treatment with concentrated inorganic acids:[32,33,71]



(LIX)

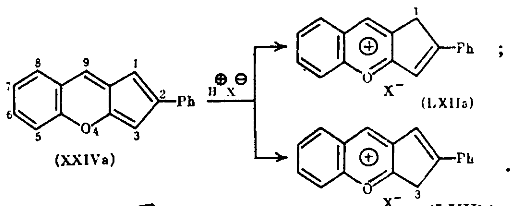
Pseudoazulenes give rise to analogous cations, but there is in this instance a possibility of the formation of two tautomeric forms (LXa, b), because the presence of the heteroatoms disturbs the molecular symmetry. The choice between these cations is of fundamental importance for the establishment of the structure of the salts formed and their derivatives and for the elucidation of the influence of the heteroatom on the electron density of the atoms in the five-membered ring:



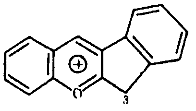
(LXa) (LXb) (LXIa) (LXIb)

According to Anderson and Harrison,[72] the [*c*]-series compounds (X = S) can be protonated in both 1- and 3-positions, but the latter pathway is preferred and for this reason the cation (LXAa, X = S) is usually formed. In the [*b*]-series compounds (X = O or NR) protonation takes place exclusively in the 1-position.[51,57,58,73]

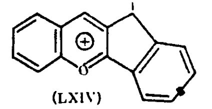
^{1}H NMR data for the pyrylium salts (LXII) have been compared[57] with the corresponding data for the salts (LXIII) and (LXIV) and it was concluded, on the basis of the study of the chemical shifts of the methylene protons (in solution in CF_3.$COOH$) in these compounds, that the protonation of 2-phenylcyclopenta[*b*]chromene (XXIVa) proceeds exclusively in the 1-position with formation of the cation (LXIIa):



(XXIVa) (LXIIa) (LXIIb)



(LXIII)



(LXIV)

The majority of pseudoazulenes are stronger bases than azulenes. The pK_a of the individual pseudoazulenes has been reported in a review[22] (the pK_a of unsubstituted azulene is 1.7). Phenyl-substituted 1*H*-pyrindines (XI) and *N*-methylcyclopenta[*b*]quinolines (XXIII) are protonated even by acetic acid, i.e. their pK_a exceeds 4.5.[51]

The basicities of azulenes and pseudoazulenes are usually characterised by the partition coefficient K_v:[32]

$$K_v = \frac{\text{pseudoazulene concentration in an inert solvent}}{\text{pseudoazulene concentration in aqueous acid}} .$$

The partition coefficient K_v has been measured as a function of the Hammett acidity function H_0 of the aqueous layer. In order to determine the basicity, it is necessary to select the value of H_0 for which the coefficient K_v becomes unity. The Hammett acidity function H_0 ($K_v = 1$) has been measured spectrophotometrically for certain pseudoazulenes containing various heteroatoms.[28] Nevertheless, we assume (in conformity with the data of Weiss and Schoenfeld[74]) that the basicities of these compounds can be determined from the value of H_0 only approximately owing to the different solubilities in the organic solvents of the compounds being compared. For this reason, the H_0 ($K_v = 1$) values can be used only to demonstrate approximately that nitrogen-containing pseudoazulenes are much more basic than oxygen- or sulphur-containing analogues and that the basicity of pseudoazulenes is higher than that of azulenes.

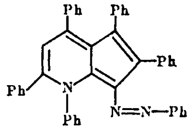
Quantitative data for the reactivities of azulenes and pseudoazulenes in relation to electrophiles have been obtained by measuring the rate of exchange of active hydrogen atoms (in the 1- and 3-positions in both azulene and pseudoazulenes) for deuterium in an acid medium.[74] The rate constant for the exchange in azulenes is lower than in 2,3; 5,6-dibenzoxalene and *N*-methyl-2,3; 5,6-dibenzopyrindine. The authors note that the rates of H–D substitution, measured in a dilute solution of CH_3COOD in CH_3OD for these pseudoazulenes as well as certain azulenes, correspond to the reactivities of these compounds predicted by Borsdorf on the basis of the π-electron densities calculated by the MO-LCAO method (see Section IV).

2. Electrophilic Substitution Reactions

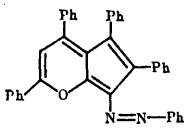
Electrophilic substitution in pseudoazulenes takes place exclusively in the 1- and (or) 3-positions (in the five-membered ring), i.e. is completely analogous to the substitution in azulenes. If both these positions in the five-membered ring are free, then in the majority of cases mixtures of mono- and di-substituted products are obtained and can be separated only by prolonged operations; the predicted preferred sites to which the reactions are directed have not been demonstrated in practice. In the majority of instances, the reactions were carried out using compounds having individually only the 1- or 3-position free. Disubstituted products have been mainly obtained for other compounds.

(a) Azo-coupling. Among inactivated aromatic benzenoid compounds, there are only a few substances capable of entering into the azo-coupling reaction with diazonium salts, whereas for azulenes this reaction is facilitated by the low localisation energy for electrophilic attack in the 1(3)-position. All the azulenes investigated hitherto readily give rise to azo-dyes.[33]

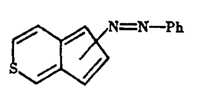
The pseudoazulenes (XIa), (XIIa), (XVI), and (XXIIIb, c) are smoothly coupled to benzene- and *p*-nitrobenzene-diazonium fluoroborates in acetonitrile[51] or in a dioxan–ethanol mixture.[58] Quaternary salts, for example (LXVIII), are formed in the first stage and on treatment with a base (sodium acetate) are converted into azo-compounds in 70–90% yield:



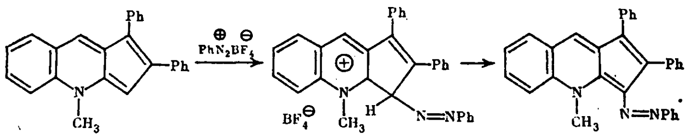
(LXV) from (XIa)



(LXVI) from (XIIa)



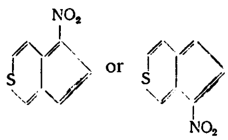
(LXVII) from (XVI)



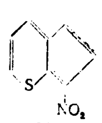
(XXIIIc) (LXVIII) (LXIX)

Azo-dyes of the type (LXIX) have the azo-group in the 3-position, while in 2-phenylcyclopenta[*b*]quinoline (XXIIIb) the azo-group can enter the 1- or 3-position. Indeed, two structurally isomeric azo-dyes have been obtained on azo-coupling, which has been demonstrated by thin-layer-chromatography (TLC); but the isomers could not be separated by crystallisation.[51]

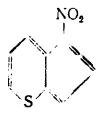
(*b*) *Nitration.* As a result of the sensitivity of pseudoazulenes to strong acids and oxidants, they cannot be nitrated by the nitrating mixture, but nitration can be readily achieved by treatment with $Cu(NO_3)_2$ in acetic anhydride or with tetranitromethane in pyridine.[26,33,34,50,61,72,75] Only mononitro-derivatives of pseudoazulenes are known; the attempts to obtain dinitro-derivatives by treatment with an excess of tetranitromethane in pyridine and also with copper or silver nitrate in acetic anhydride were unsuccessful.[72] The synthesis of nitropseuduazulenes has been described: 3-nitro-1,2,5,7-tetraphenylcyclopenta[*b*]pyran and 3-nitro-1,2;5,6-dibenzoxalene as well as 1(3)-nitrocyclopenta[c]thiapyran (LXX).[61,72] It has been noted that the properties of the product (LXX) preclude a choice between the structures of the 1- and 3-substituted derivatives:



(LXX)

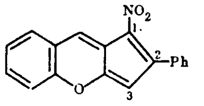


(LXXI)

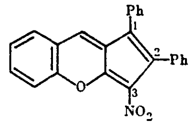


(LXXII) .

On nitration with an excess of tetranitromethane in pyridine, cyclopenta[*b*]thiapyran (XIII) affords two isomeric products (LXXI) and (LXXII), whose structures have not been determined unambiguously. However, it has been established that the reaction of 2-phenylcyclopentachromene (XXIVa) with $C(NO_2)_4$ in pyridine leads exclusively to the 1-nitro-derivative (LXXIII), while the 1,2-diphenylcyclopentachromene is nitrated, as expected, in the 3-position:[75]



(LXXIII)



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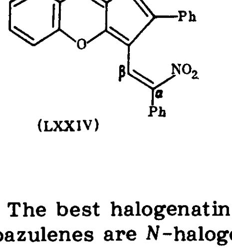
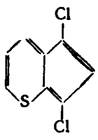
The 3-*trans*-styryl derivative of 1,2-diphenylcyclopentachromene is capable of being nitrated at the α-carbon atom of the styryl residue, i.e. in the position most remote from the cyclopentachromene ring and at the same time conjugated with it (the vinylogy principle),[76] forming the nitrostyryl derivative (LXXIV):

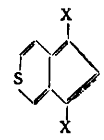


(LXXIV) .

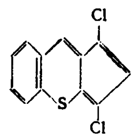
(*c*) *Halogenation.* The best halogenating agents for azulenes[33] and pseudoazulenes are *N*-halogenosuccinimides, whose use makes it possible to obtain mono- and di-halogeno-derivatives in high yields (up to 82%).[26,34,38,50,58,61,72]



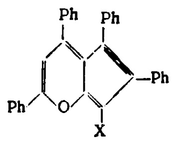
(LXXV)



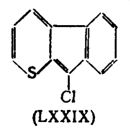
(LXXVI a, b)



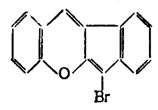
(LXXVII)



(LXXVIIIa, b)



(LXXIX)



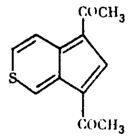
(LXXX)

a:X=Cl
b:X=Br

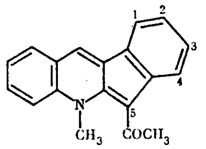
The halogenation of pseudoazulenes without substituents in the 1- and 3-positions yielded the disubstituted products (LXXV),[34] (LXXVIa,b),[61,72] and (LXXVII).[38] The monosubstituted pseudoazulenes (LXXVIIIa, b),[58] (LXXIX),[34] and (LXXX)[26,50] have also been obtained with the aid of *N*-halogenosuccinimides. The attempt to obtain the trichloro-derivatives from cyclopenta[c]thiapyran (LXXVIa) leads only to a polymeric material,[72] while 1,3-dichloroazulene is capable of being chlorinated by *N*-chlorosuccinimide with formation of 1,3,5-trichloroazulene in 17% yield.[77]

(*d*) *Acylation and formylation.* It is known that azulenes are acylated by carboxylic acid chlorides in the presence of aluminium chloride, perchloric acid, or tin tetrachloride with formation of 1-mono- and 1,3-di-acyl derivatives. The reaction with $(CF_3CO)_2O$ takes place almost quantitatively without a catalyst.[33] Azulene has been acylated with the chlorides or bromides of oxalic, malonic, and phenylacetic acids.

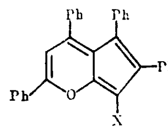
However, none of these methods are very applicable to pseudoazulenes owing to their greater basicity and lower chemical stability. 1,3-Diacetylcyclopenta[c]thiapyran (LXXVIc) has been obtained in only 9% yield by the acylation of compound (XVI) with acetic anhydride in the presence of $SnCl_4$:[61,71]



(LXXVIc)

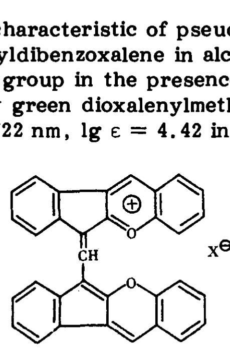


(XXVIIId)



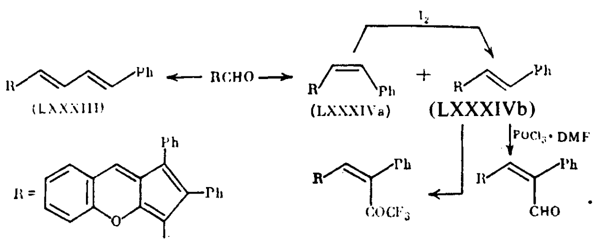
(LXXXI): X=CHO

5-Acetyl-*N*-methyl-1,2;5,6-dibenzoazalene (XXVIIId) has been obtained by reaction with acetic anhydride without a catalyst.[52] The Vilsmeier–Hack reaction is most often employed to synthesise formyl derivatives.[26,50,52,58] Both mono- and di-formylazulenes have been obtained from azulenes by this method.[33] The aldehyde (LXXVI) has been obtained by formylating compound (XIIb) by the complex $POCl_3.DMF$ with isolation of the intermediate phosphorodichloridate $[X = CH = N^+(CH_3)_2.PO_2Cl_2^-]$ in a high yield. The 1,3-dialdehyde has been obtained in 70% yield by heating 2-phenylcyclopentachromene with an excess of the Vilsmeier reagent.[75] The thermal acylation of compound (XXIVa) with malonic acid in the absence of solvents leads to the 1-acetyl derivative.[78] Under mild conditions (treatment with oxalyl bromide in CCl_4 for many days at 20 °C), the pseudoazulenes (XIII), (XXVIII), and (XXIX) form substituted glyoxylic acids, which are decarbonylated to the corresponding carboxylic acids on heating to 70 °C.[79,80] It has been shown[26,52] that a high basicity and ready hydrolytic elimination of the formyl group on heating in the presence of inorganic acids are characteristic of pseudoazulene aldehydes.[26,52] 3-Formyldibenzoxalene in alcoholic solutions[26] splits off the formyl group in the presence of $POCl_3$ and affords the intensely green dioxalenylmethane derivative (LXXXII) (λ_{max} = 722 nm, $\lg \varepsilon = 4.42$ in methanol).

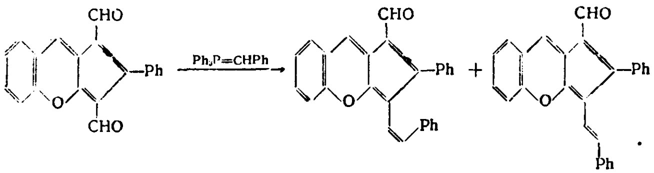


(LXXXII)

The same compound can be obtained from dibenzoxalene and 3-formyldibenzoxalene, analogously to the synthesis of the diazulenylmethane dye obtained by condensing azulene with 1,4-formylazulene.[33] Pseudoazulene aldehydes can be used for the synthesis of other derivatives, for example, polyene derivatives. Thus a series of styrylpseudoazulenes have been obtained by the Wittig reaction[76] from mono- and di-formylcyclopentachromenes. The virtually pure *trans*, *trans*-isomer (LXXXIII) has been obtained by reaction with cinnamylidenephosphorane, while the reaction with benzylidenephosphorane produced the *cis*- and *trans*-isomers (LXXXIVa,b) in proportions of approximately 1 : 2. The *cis*-isomer (LXXXIVa) is converted quantitatively into the *trans*-isomer on treatment with catalytic amounts of I_2 by analogy with the isomerisation of *cis*-*1*-styrylazulene:[81,82]



Compound (LXXIVb) can undergo the electrophilic substitution reaction in the CH=CH–Ph side group (in the α-position in the styryl residue). The increased electron density at the C(1) atom of the 2-phenylcyclo pentachromene system affects the structural selectivity of the Wittig reaction for the 1,3-dialdehyde, which reacts with one equivalent of $Ph_3P{=}CHPh$ to produce the *cis*- and *trans*-3-styrylaldehydes (LXXVa) and (LXXXVb):

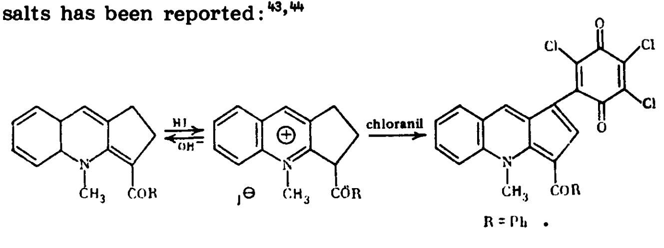


(LXXXVa) (LXXXVb)

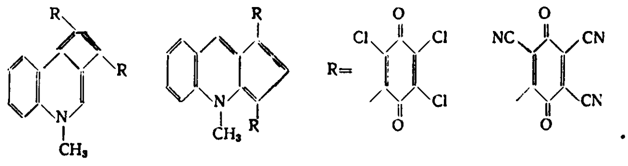
(e) Reactions with organic π-acids. The reaction of 7,7,8,8-tetracyanoquinodimethane (TCQD) with azulenes leads to the formation of products of the 1,6-addition to the quinonoid bond system of TCQD as a result of the initial one-electron oxidation of the donor by the acceptor,[83] exactly as in the reaction of azulenes with tetracyanoethylene.[84,85]

Pseudoazulenes also readily form π-complexes with various acids: trinitrobenzene, picric acid, etc.[7,14,27,32,33] The complexes with trinitrobenzene are frequently used to purify, identify, and isolate unstable pseudoazulenes; these complexes readily decompose into their components in chromatography.

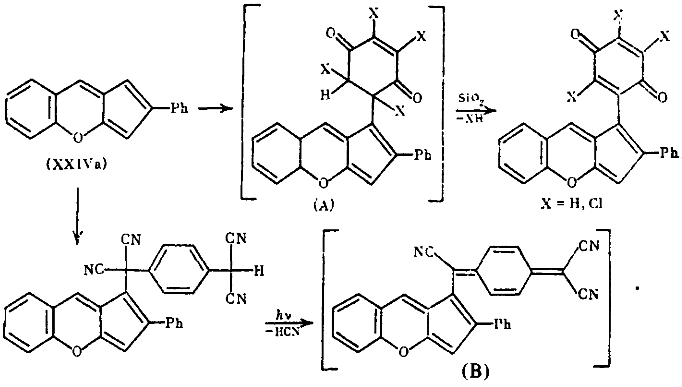
The formation of 1-(3,5,6-trichloro-1,4-benzoquinon-2-yl)-3-benzoyl-4-methyl-4*H*-[*b*]quinindine in 64% yield using chloranil as the dehydrogenating agent for quaternary salts has been reported:[43,44]



The following disubstituted derivatives were later obtained on dehydrogenation of the quaternary salts of hydrogenated pseudoazulenes:[29,45,46]

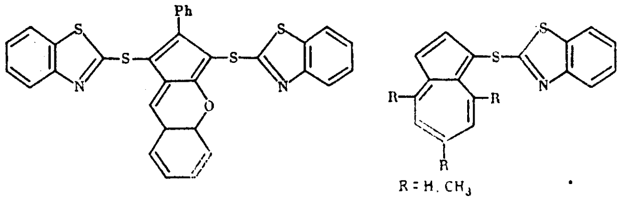


The high reactivity of the 1-position in compound (XXIVa) enables it to participate in reactions involving addition to organic π-acids, for example, to benzoquinone, chloranil, and TCQD, with the ultimate formation of products resulting from the substitution of hydrogen, chlorine, or a CN group. However, the products (A) and (B) proved to be unstable and could not be isolated in a pure state:[86]

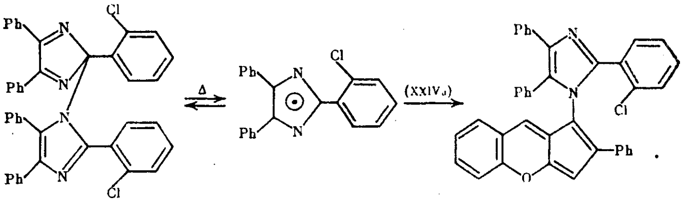


3. Homolytic Substitution

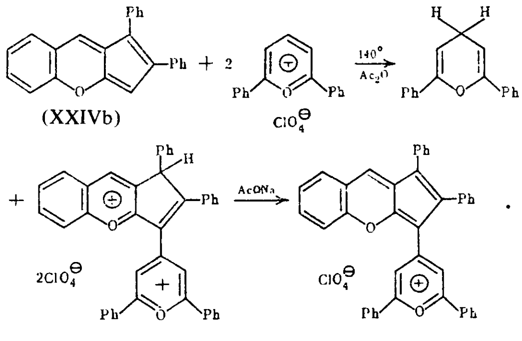
The majority of radical substitution reactions have been thoroughly investigated for azulene derivatives.[31–33,87] Pseudoazulenes, which are no less reactive than azulenes, should also enter into similar reactions, but the literature data on this topic are extremely limited.[22] It is known only that radical species such as 2-benzothiazolylsulphenyl, 2-(*o*-chlorophenyl)-4,5-diphenylimidazolyl, and 2,6-diphenyl-4*H*-4-pyranyl, formed at elevated temperatures, react with compound (XXIVa).[88] When the latter is fused with 2,2-dibenzothiazolyl disulphide (at 200 °C), 1,3-di(benzothiazolylthio)cyclopenta[*b*]chromene is formed in 12% yield; the formation of the mono-substituted benzothiazolylthio-derivative was not then observed, while in the reactions with azulene and 4,6,8-trimethylazulene, only the 1-substituted derivatives were obtained:[89]



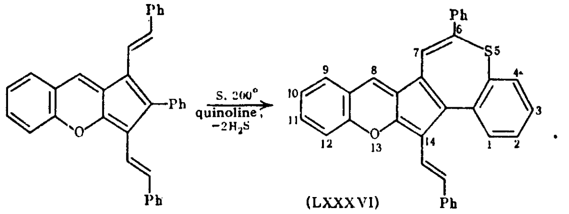
The thermal reaction of 1,2-bis[2-(*o*-chlorophenyl)-4,5-diphenylimidazolyl] with 2-phenylcyclopenta[*b*]chromene leads to the formation of the 1-substituted derivative, as in the reaction with azulene:[90]



The reaction of compound (XXIVb) with 2,6-diphenylpyrylium perchlorate in boiling acetic anhydride leads to the formation of 2,6-diphenyl-4-{1,2-diphenylcyclopenta[*b*]-3-chromylia}pyrylium diperchlorate in 75% yield.[91] It has been suggested that the primary step in this reaction is the one-electron oxidation of the substrate by the 2,6-diphenylpyrylium cation, which leads to the formation of the extremely reactive 1,2-diphenylcyclopenta[*b*]chromenylium radical-cation and the 2,6-diphenyl-4*H*-4-pyranyl radical, which recombine to a doubly charged primary cation:



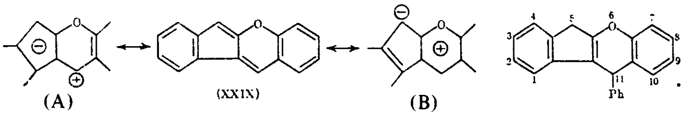
An analogous reaction has been carried between 2,6-diphenylpyrylium perchlorate and 6-heterylazulenes.[92] Other organic compounds with an enhanced electron density at, at least, one of the carbon atoms (*NN*-dimethylaniline[93,94] and 1-methyl and 2-methyl-indoles[95,96]) or substances capable of being readily oxidised to readily stable radical-cations (ferrocene[97]) can also serve as substrates in this reaction. An example of the transmission of the influence of the electron density to the non-benzenoid aromatic ring on the reactivity of the conjugated side chain (vinylogy) is provided by the reaction of 2-phenyl-1,3-distyrylcyclopentachromene with sulphur, which leads to a new heterocyclic system: 6-phenyl-14-styrylbenzo[2',3']thiepino[4',5';2,1]cyclopenta[*b*]chromene (LXXXVI) in 40% yield:[76]



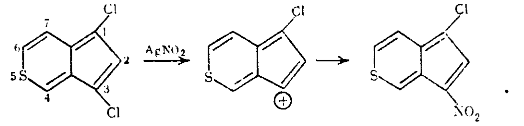
(LXXXVI)

4. Nucleophilic Substitution

The effect of alkyl- and aryl-lithium has been investigated on the pseudoazulene systems (XVIII), (XXIV) and (XXIX).[16,45,46] The hydrocarbon residue then attacks the carbon atom located opposite to the heteroatom. Dihydro-compounds, which can be again dehydrogenated to pseudoazulenes, are obtained by hydrolysing the intermediates. Such reactions are characteristic of π-deficient heterocycles. The system (XXIX), which is isoelectronic with azulene, can be described as a hybrid of resonance structures—those of the pyrylium cation (B) and the anion (A):



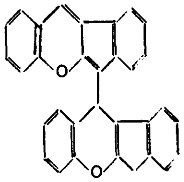
The limiting form (A) is responsible for the sensitivity of dibenzoxalene (XXIX) to nucleophiles, which has been conformed by its reaction with phenyl-lithium, leading to 11-phenyl-5,11-dihydrodibenzoxalene. Dibenzoxalene (XXIX) is resistant to lithium malonate and maleic anhydride; the attempts to replace the oxygen heteroatom by sulphur and nitrogen proved unsuccessful.[26] It is also known that only one chlorine atom, located at the C(3) atom, in 1,3-dichlorocyclopenta[c]thiapyran is substituted by silver nitrite:[72]



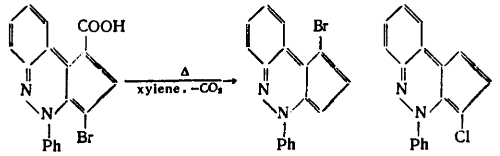
5. Other Reactions of Pseudoazulenes

Apart from the reaction described above, isothialene (XVI) has been substituted by thiocyano-groups using thiocyanogen, which led to 1,3-dithiocyanocyclopenta[c]thiapyran.[61,72] The reaction with $Cu(SCN)_2$ in acetonitrile yielded 1,2-diphenyl-3-thiocyanocyclopenta[*b*]chromene,[98] while that with $Cu(SO_2Ph)_2$ afforded benzenesulphonyl derivatives of 1,2-diphenyl- and 2-phenylcyclopenta[*b*]chromene.[75]

The alkylation of 1,2,5,7-tetraphenylcyclopenta[*b*]pyran with t-butyl chloride in the presence of aluminium chloride has been carried out successfully.[58] Inorganic acids and phosphoryl chloride induced the dimerisation of dibenzoxalene (XXIX) with formation of a dimer having the following structure:[53]



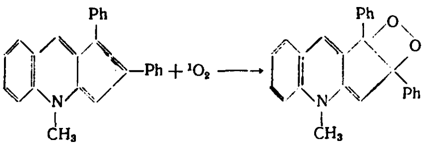
An instance of allylic rearrangement has been described in relation to 4-phenyl-4*H*-cyclopenta[*c*]cinnoline.[99] On being refluxed in xylene, 3-bromo-4-phenyl-4*H*-cyclopenta[*c*]-cinnoline-1-carboxylic acid (LXXXVIII) is decarboxylated with a simultaneous rearrangement, leading to the formation of the bromo-derivative (LXXXVIII):



(LXXXVII) (LXXXVIII) (LXXXIX)

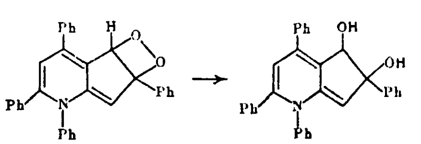
In contrast to the bromoacid (LXXXVII), the corresponding chloroacid is decarboxylated under the same conditions without a rearrangement, forming the chloro-derivative (LXXXIX). It is noteworthy that the decarboxylation of the bromoacid (LXXXVII) leads only to the bromo-derivative which can be obtained by brominating 4-phenyl-4*H*-cyclopenta[*c*]cinnoline by *N*-bromosuccinamide.

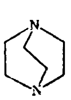
The photosensitised pseudoazulene oxidation processes have been examined.[100] Polyarylcyclopenta[*b*]quinolines, for example, compound (XXIIIc), 1-pyrindines (XI), and cyclopenta[*b*]chromenes sensitise the formation of singlet oxygen on irradiation in air in various solvents and are oxidised by it to dioxetans, which readily decompose with chemiluminescence. Dioxetans also generate $^1O_2$, as a result of which the oxidation reactions undergo self-acceleration:



(XXIIIв) (XC)

The formation of the dioxetan having the structure (XC) has been suggested. The thermal decomposition of the dioxetan (XCI) leads to dihydroxy-compound (XCII):



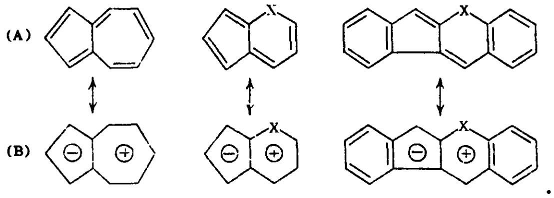


(XCI) (XCII) 10% (XCIII)

The photodecolorisation is retarded in the presence of a typical $^1O_2$ quenching agent—diazabicyclo-octane (XCIII), or a chemical quenching agent—2,5-dimethylfuran, which forms a peroxide. The quantum yields in the decomposition of pseudoazulenes are approximately 2×10^{-3}.

IV. QUANTUM-CHEMICAL CALCULATIONS

The aromaticity of pseudoazulenes is determined by the sextet of π-electrons in the heterocyclic ring, made up of the single unshared electron pair of the heteroatom, located in the *p* orbital axial in relation to the plane of the ring, and four π-electrons of the double bonds. The aromatic sextet of electrons in the five-membered ring is obtained as a result of the possibility of polarisation in the direction from the six-membered ring to the five-membered ring, the conditions in both rings approaching those of an aromatic sextet. For this reason the dipolar structure makes a significant contribution to the electronic structure of pseudoazulenes. The azulene[32] and pseudoazulene[35,38] systems can be represented by resonance hybrid structures, intermediate between the Kekulé form (A) and the dipolar form (B).



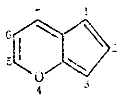
The data for electron distribution obtained for pseudoazulenes by the LCAO-MO method in terms of the Hückel approximation[57,101–110] and by the Pariser–Parr–Pople (PPP) method,[98,101] the reactivity data, and the electronic absorption spectra indicate an azulene-like behaviour of representatives of this class of non-benzenoid non-alternant aromatic compounds. Despite the difficulties associated with the allowance for the contribution by polar structures, the electron deficiency in the six-membered ring and the excess electron density in the five-membered ring have been calculated for all the pseudoazulenes. It follows from the molecular diagram for indolizine that a considerable positive charge is localised on the nitrogen atom and that there is a negative charge on all the carbon atoms except the C(8) atom (six-membered ring).[112] Since different workers have used different sets of parameters, the calculated electron density distributions on the carbon atoms could not be compared directly. The results yielded by the same set of parameters for different systems lead to the following conclusions: the electron density on the carbon atoms decreases from the nitrogen-containing pseudoazulenes to the oxygen-containing compounds as a consequence of the greater electronegativity of oxygen. In the [*b*]-series of pseudoazulenes the carbon atoms of the five-membered ring have a higher electron density than for the [*c*]-series. The presence of a condensed aromatic ring in the 1,2-positions increases the electron density in the five-membered ring, while condensation in the 5,6-positions reduces it. The distribution of electron density on the individual atoms of the five-membered ring is as follows: the 1- and 3-positions have an increased electron density compared with that in the 2-position. In the [*b*]-series the C(1) atom is more electron-deficient than the C(3) atom,[22,98] while in the [*c*]-series the situation changes. In azulene, the 1- and 3-positions are equivalent as a consequence of the symmetry of the molecule, while the 2-position is much more electron-deficient as in pseudoazulenes.[32] The self-consistent field calculations for the azulene molecule[113,114] yielded a somewhat different picture. On average, the five-membered ring carries an excess negative charge, as before, but, in contrast to the result yielded by the simpler Hückel MO method, the atom in the 2-position carries a positive charge.

Electrophilic substitution of non-condensed representatives of pseudoazulenes (XI)–(XVI) is directed preferentially to the 1- or 3-position. If both these positions are free, then they can be attacked simultaneously. Attack by nucleophiles should take place in the 7-position for representatives of the [*b*]-series and in the 4-positions for the [*c*]-series. Radical reactions are directed to the 5-position for the [*b*]-series, while representatives of the [*c*]-series react in the 4-position.[108] Various preferred positions for electrophilic, nucleophilic, and radical substitution reactions follow from the localisation energies A_r, the π-electron densities q_r, or the free valence indices F_r for the individual C atoms. The reactivities of the C atoms of cyclopenta[*b*]pyran (XII) are presented in Table 2.[104]

Table 2. Preferred mode of substitution in the oxalene (XII)*.

Electrophilic substitution		Nucleophilic substitution		Radical substitution		Electrophilic substitution		Nucleophilic substitution		Radical substitution	
$A_r^{\ominus}$	q_r	$A_r^{\ominus}$	q_r	$A_r^{\odot}$	F_r	$A_r^{\oplus}$	q_r	$A_r^{\ominus}$	q_r	$A_r^{\odot}$	F_r
1	3	5	5	5	5	5	6	1	2	3	3
3	1	7	7	1	7	6	7	3	1	2	2
2	2	2	6	7	1	7	5	6	3	6	6

*The reactivity diminishes on moving towards lower rows.



(XII)

It follows from the calculations of the electronic absorption spectra by the Hückel MO method[101,102,104,107] and the PPP method[98,111] that, analogously to azulenes, the long-wavelength band in the range 500–700 nm corresponds to the $S^0 \rightarrow S^1$ transition, while the band in the range 360–390 nm corresponds to the $S^0 \rightarrow S^2$ transition. The absorption in the short-wavelength part of the spectrum is determined by complex transitions. The long-wavelength transition is accompanied by charge transfer preferentially from the five-membered ring to the six-membered heterocycle. Thus the overall negative charge on the atoms of the five-membered ring in 2-phenylcyclopentachromene is reversed on transition to the first excited state (+0.096 against −0.374 in the ground state), while that in the heterocycle diminishes appreciably (to +0.008 against +0.315). The bonds in the rings become to a large extent equalised. The comparatively low intensity of the band can be accounted for by the small change in the dipole moment of the transition ($\Delta\mu = 0.40$ D). Theoretical analysis of the long-wavelength electronic transition has shown that it is determined mainly by the fulvene group, which is a constituent fragment of the pseudoazulene molecule.[98]

It has been demonstrated theoretically[52,111] that the influence of the heteroatom on the absorption spectra of heterocyclic pseudoazulenes is very insignificant. According to a quantum-chemical calculation, the influence of substituents on the energy of the long-wavelength transition is the same as that for azulenes.[108] A bathochromic or hypsochromic shift of the long-wavelength band, induced by the introduction of alkyl groups in different positions in the azulene ring (the Plattner rule), is especially typical for azulenes.[115] The influence of the methyl group in different positions in cyclopenta[*c*]pyran has been calculated[102] and it has been shown that the Plattner rule should hold also for pseudoazulene systems. Inadequate experimental data make it impossible to confirm this postulate.

V. PHYSICOCHEMICAL PROPERTIES

1. Stability

Pseudoazulenes are in most cases deeply coloured, crystalline, weakly basic compounds, which dissolve in aqueous solutions of strong acids with loss of the characteristic colour and are reprecipitated unchanged on dilution with water or aqueous bases and can thus be extracted from organic solvents. In terms of their colour, basicity, and resistance to alkalis, they resemble azulene. In contrast to the majority of azulenes, numerous pseudoazulenes are unstable. Simple unsubstituted representatives of certain systems cannot be isolated in a pure form at all. Phenyl substituents stabilise the system and polyaryl-substituted compounds can be stored for a long time at room temperature without appreciable decomposition. Thus *N*-methyl derivatives of unsubstituted 1-pyrindine,[58] cyclopenta[*b*]quinoline,[45,46] and indeno[1,2-*b*]-pyridine[27] are unstable, while 1-phenyl and 1,2-diphenyl-cyclopenta[*b*]quinolines as well as the tri- and tetra-phenyl derivatives of 1-pyrindine are comparatively stable.[51] Substitution by even one strong electron-accepting substituent is sufficient to achieve the complete stabilisation of the unstable systems. "Picrylation" has an especially powerful stabilising effect.[116] The stability decreases very markedly on passing from sulphur- and nitrogen-containing systems to the oxygen analogues; thus cyclopentathiapyran and 2*H*-pyrindine were synthesised a long time ago,[36,37] while cyclopentapyran is still unknown. The [*c*]-series pseudoazulene systems are more stable than compounds of the [*b*]-series. Cyclopenta[*b*]thiapyran has been isolated in the form of an extremely unstable blue oil;[15] in contrast to this, cyclopenta[*c*]thiapyran[43] is a fairly stable crystalline substance. Under the influence of atmospheric oxygen and light, many pseudoazulenes decompose very rapidly. Solutions in non-polar solvents are preserved for a long time, while in polar solvents, especially in methanol, decomposition is observed over a period of 4–5 h.[51] The stability of pseudoazulenes in relation to bases makes it possible to chromatograph them on alumina.

2. Electronic Absorption Spectra

There is no doubt that the long-wavelength absorption, observed for azulene in the region of approximately 600 nm, is most characteristic for the identification of the compounds considered. Only an indirect comparison of the spectra of pseudoazulenes with those of carbocyclic analogues is possible, since the corresponding polyphenylazulenes and certain polycyclic condensed systems are so far unknown, while many pseudoazulene systems without substituents are unstable. The electronic spectra of 1,2-, 4,5-, and 5,6-benzoazulenes have been compared with those of unsubstituted azulenes.[117–125] Since azulenes phenyl-substituted in the seven-membered ring have the same absorption spectrum as unsubstituted azulenes,[126,127] El'tsov et al.[51] compared the spectra of pyrindines with those of 2-phenylazulene.[128] The comparison showed that the long-wavelength band in the spectra of non-condensed 1-pyrindines has undergone a hypsochromic shift by 60–70 nm compared with the spectra of azulene. Substituents at the nitrogen atom have little influence on the long-wavelength transition and hardly affect the short-wavelength transitions. Pyrindines absorb in approximately the same part of the spectrum as the corresponding oxygen analogues. The influence of phenyl substituents on the direction and magnitude of the shifts of the absorption maxima[16,27,28,48,57] is approximately the same as for azulene. The phenyl group in the 1- or 3-position in cyclopenta[*b*]quinoline induces a 22 nm bathochromic shift (there is a 26 nm shift in the spectrum of azulene[128]). In the oxygen analogue—2-phenylcyclopenta[*b*]chromene—the successive introduction of phenyl substituents into the five-membered ring leads to a bathochromic shift of the long-wavelength band by 42 nm for one phenyl group (the calculated shift is thus 28.2 nm) and by 60 nm for two such groups. The *trans*-styryl group in the 1-position induces a +80 nm shift, while that in the 3-position induces a 60 nm shift. Two *trans*-styryl groups cause a "red" shift by 140 nm without an appreciable change in the oscillator strength.[98] Electron-accepting substituents in the five-membered ring of 4*H*-indeno[2,1-*b*]quinoline cause a hypsochromic shift of the absorption by 30–35 nm, while in the spectrum of the oxygen analogue the shift is by only 5–10 nm.[52] The introduction of electron-accepting substituents in the 3-position in 1,2-diphenylcyclopenta[*b*]chromene results in a hypsochromic shift of the long-wavelength band by approximately 30 nm with an increase of the oscillator strength by a factor of 1.5. The same substituents in the 1-position induce a 10–30 nm bathochromic shift and an increase of the oscillator strength of the band by a factor of 4–5,[98] in contrast to azulene, where a hypsochromic shift is observed exclusively.[31]

The emission spectra of azulene are known to be unusual:[129–132] the fluorescence of azulene and its derivatives corresponds to a very rare $S^2 \rightarrow S^0$ type of transition. Such anomalous luminescence is probably a consequence of the marked splitting of the S^2 and S^1 levels and a greater mutual approach of the S^1 and S^0 levels than for other aromatic systems. It has been found[51,53] that the luminescence of pseudoazulenes is just as anomalous as for azulenes. The quantum yields are 10^{-4}–10^{-5} against 10^{-2} for azulene.[130] As for azulene, the authors did not observe phosphorescence in pseudoazulenes. The structure of the electronic spectra and the luminescence properties of 1,2-benzoxalene derivatives have been examined.[134]

3. Infrared, ^{1}H NMR, and Mass Spectra

Virtually no systematic studies of the IR, ^{1}H NMR, and mass spectra of pseudoazulenes are described in the literature. These data are usually given in the experimental parts of synthetic studies.

The IR spectra of substituted pseudoazulenes contain only insignificant characteristic bands corresponding to the normal absorption of aromatic rings. For example, the spectra of indeno[2,1-*b*]benzopyrans in the range 1560–1660 cm^{-1} have four bands due to the vibrations of the aromatic ring and the C=C stretching vibrations and the moderately intense band at 1230 cm^{-1} has been attributed to the ν(C=O) deformation vibrations of the –C=C–O group.[26] The vibration frequencies of the substituents in the five-membered ring in both azulene and pseudoazulenes are appreciably reduced.[31,58,134,135] If the system contains the CN, CHO, or $COCH_3$ groups in the five-membered ring, then the latter, being substituents of the second kind, promote the polarisation of the system with formation of the structure (B). The ν(C=O) vibration frequencies in the aldehydes (1611 cm^{-1}) and ketones (1598 cm^{-1}) derived from indeno[2,1,*b*]quinoline (XXVIII) are reduced compared with the frequencies in the similar derivatives of indeno[2,1-*b*]benzopyran (XXIX) (1631 cm^{-1} in the aldehydes and 1625 cm^{-1} in the ketones),[103] which can be explained by the smaller electronegativity of the nitrogen atom compared with the oxygen atom, which promotes the formation of a polar structure. In the IR spectrum of 1,3-diacetylcyclopenta[*c*]thiapyran the stretching vibrations at the carbonyl group appear at 1629 cm^{-1}, i.e. at longer wavelengths than the corresponding vibrations of the carbonyl group in 1,2-diacetylazulene, observed at 1638 cm^{-1}.[72] The dependence of the ν(C=O) vibration frequency on the position of the CO group in azulene has been indicated.[136] The authors note that the spectra of 1-phenylacetyl- and 2-phenylacetyl-azulenes contain the absorption bands due to the carbonyl group at 1640 and 1675 cm^{-1} respectively. In the spectra of 1-carbonyl-containing pseudoazulenes of the cyclopenta[*b*]chromene series there is a possibility of the overlap of the frequencies of the aromatic C=C and C=O bonds. The possibility of using the integral intensities of the vibration bands of the bonds and ^{13}C NMR to demonstrate the presence of carbonyl groups has been examined.[137] ^{13}C NMR spectrum of 1,3-diformyl-2-phenylcyclopenta[*b*]chromene in $CDCl_3$ shows two signals with chemical shifts δ of 186.61 and 183.77 p.p.m., corresponding to the carbon atoms of the two formyl groups, and also the signals of the phenyl substituent in the region of 77.25 p.p.m. and the remaining carbon atoms at 118.27–138.86 p.p.m. A considerable upfield shift of the ^{13}C resonance signal of the C=O group compared with acetophenone (196.9), benzaldehyde (190.7), and acetone (204.1) has been noted.[138] It follows from the comparative analysis of the shifts δ of the CHO groups in the ^{13}C NMR spectra, the ν(C=O) frequencies, and the integral intensities of the absorption bands due to the stretching vibrations of the C=O groups in the IR spectra that the CHO groups in the 1- and 3-positions in azulene and cyclopenta[*b*]chromene are strongly polarised, which is comparable to the polarisation of the C=O group in benzotropones.[139] The ^{13}C NMR spectra of unsubstituted azulene and mono- and poly-methylazulenes have been published.[140] The chemical shifts of the methyl groups in different positions in the azulene ring are in the range δ = 12.6–28.5 p.p.m., while the shifts for the C_1–C_{10} atoms are in the range δ = 116–146.9 p.p.m.

The ^{1}H NMR spectrum of azulene[141,142] agrees well with its structure. The ^{1}H NMR spectrum of cyclopenta[*c*]thiapyran has been interpreted.[61] The spectra of its methyl derivatives were examined by Radeglia and Wagner[64] and those of the 1-pyrindine system were considered by Anastassion and Reichmanis.[143] The protons in the 1-, 2-, and 3-positions in azulene are not shielded to the same extent as the corresponding protons in cyclopenta[*c*]thiapyran. It follows from this that the polar structure of pseudoazulenes has a stronger influence on the distribution of electron density in the ground state.[61] The different degrees of shielding of the individual protons in the pseudoazulene nuclei, which should be expected on the basis of calculated data as a consequence of the differences in electron density, do indeed follow from the ^{1}H NMR spectra of these compounds, for example, cyclopenta[*b*]quinoline.[29,43–46] In the ^{1}H NMR spectra of cyclopenta[*b*]pyrylium salts obtained by protonating cyclopenta[*b*]pyran (XII), cyclopenta[*b*]chromene (XXIV), and indeno[2,1-*b*]chromene (XXIX) by $HClO_4$, the signal of the methylene group appears in the range δ = 4.48–4.77 p.p.m. (in CF_3COOH).[57] In the spectrum of the protonated form of 4,6,8-trimethylazulene (in 96% H_2SO_4), the signal of the C(1)H_2 methylene group is observed at 3.56 p.p.m. The strong deshielding influence of the electron-accepting groups $PhSO_2$, CH_3CO, and CF_3CO in the 1-position [the substituted C(1) atom of the trimethylazulene system is protonated] causes a downfield shift of the C(1)–H signal (5.85, 5.40, and 4.80 p.p.m. respectively).[144,145–149] 2-Alkyl derivatives of 6-, and 7-, and 8-ethoxycarbonylindolizines are protonated at the C(3) atom, the protons of the methylene group formed in this process being manifested by a signal at 5.28 p.p.m. with an intensity equivalent to two proton units. The presence of the CHO, NO_2, and $COCH_3$ substituents in the 3-position (in contrast to the 4,6,8-trimethylazulene molecule) alters the centre subjected to protonation, which is directed in this instance to the oxygen atom of the substituent.[150–153]

There are no literature data on the mass spectra of pseudoazulenes containing one heteroatom, although the mass spectra of compounds with several heteroatoms confirm the aromatic character of pseudoazulenes.[23,76,154,155] As for other aromatic compounds, the principal peak is identical with that of the molecular ions; the spectra contain numerous doubly charged ions; there is a small number of low-intensity fragment peaks.

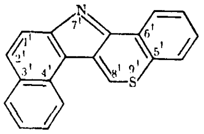
4. The Dipole Moment

Since the five-membered ring is enriched in electrons, the azulene molecule has a dipole moment, the five-membered ring being the negative end of the dipole. The dipole moment of azulene (6.9 D) has been calculated from the electron densities and C–C bond orders; direct measurement yielded 1.04 ± 0.05 D.[156] The theoretical value calculated in terms of the simple MO-LCAO approximation differs very markedly from the above value. However, improved calculations have shown that the charge distribution in azulene is more uniform and the dipole moment is therefore appreciably smaller than the value predicted by the simple MO theory. For example, application of the MO method with allowance for configuration interaction led to 1.88 D.[157] The value closest to the experimental dipole moment (1.33 D)[158] has been obtained by the self-consistent field calculation using variable electronegativities. Improved methods of calculation have shown that the π-electron density at the 2-atom is less than unity, while at the 5- and 7-atoms the densities are more than unity, as a result of which the dipole moment is appreciably reduced.

Pseudoazulenes should possess a dipole moment greater than that of azulene. The measured dipole moment of 5-methyl-5*H*-indeno[2,1-*b*]quinoline is 2.35 D and that of 1,2;5,6-dibenzoxalene is 2.02 D. The substituents in pseudoazulenes have a striking influence, which exceeds the normal values. When electron-accepting substituents (CN, CHO, and $COOC_2H_5$) are introduced into the five-membered ring of 1,2;5,6-dibenzoxalene, the dipole moment increases much more than might have been expected on the basis of the group moments of the substituents.[103] This can be explained by the considerable contribution of the polar structure (B). This contribution is greater the more electronegative the substituent and the greater the polarisability of the pseudoazulene. The dipole moment and the polarisability of azulene in the ground state as well as in the first and second excited states have been examined.[159]

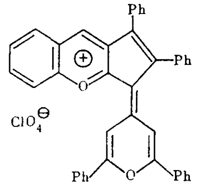
VI. BIOLOGICAL ACTIVITY AND PRACTICAL APPLICATIONS OF PSEUDOAZULENES

Like azulene derivatives, pseudoazulenes have a distinct biological activity. Certain alkylindolizines have a physiological activity analogous to convulsing poisons and induce the paralysis of the muscular and respiratory activity.[160] The Mannich bases obtained from 2-phenyl and 1,2-diphenylindolizines have a depressing influence on the central nervous system.[161–166] Derivatives of indolizine-1-acetic acid have been patented as analgesic and anti-inflammatory agents.[167,168] 2-Furylindolizines exhibit an antimicrobial activity,[169] while 6-methyl-7-(2,4,5-trimethylbenzyl)-2-phenylindolizine shows growth regulating activity.[170,171] The influence of 6*H*-pyrrolo[3,2-*f*]indolizines[172–174] on the cardiovascular system, arterial pressure, and pulse has been investigated; the application of the hydrochloride of 2-ethoxycarbonyl-4-isobutyl-3,6,7,8-tetramethyl-6*H*-pyrrolo[3,2-*f*]indolizine as an antiarrhythmic agent,[175] whose effect is several times greater than that of other antiarrhythmic agents such as quinidine and novocainamide, has been patented. Certain pseudoazulenes exhibit an antitumour activity.[176–179] The carcinogenic activity of condensed polycyclic pseudoazulenes containing the nitrogen and sulphur heteroatoms has been studied. Dibenzo[3,4,5,6]thiapyrano[4,3-*b*]indolenine (XCIV) exhibited the maximum carcinogenic activity:[180]



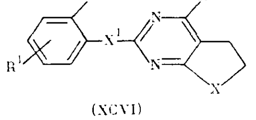
(XCIV)

It has been established that 2-arylindolizines possess no carcinogenic activity.[181] Liquid crystal derivatives of azulene have been obtained recently.[182] 2,6-Diphenyl-4*H*-4-{3*H*-1,2-diphenylbenzo[*b*]cyclopenta[*e*]-3-pyrania}pyrylium perchlorate (XCV) has been proposed as a sensitiser of photoconductivity in order to extend the range of the spectral sensitivity of electrophotographic materials to 800 nm:[183]

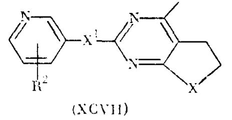


(XCV)

Sulphonamide derivatives of hydrogenated pseudoazulenes of the (XCVI) and (XCVII) types with the following substituents have been patented as herbicidal preparations:[184] R = H, Me, MeO, Hal, NO_2, CF_3, COOAlk, SO_2Alk, OSO_2R, $CF_3CH_2O_3S$, or MeN(OMe)SO_2; R^1 = H, Hal, Alk, or MeO; R_2 = H, Hal, Alk, AlkO, NO_2, COOAlk, or AlkS; R^3 = H, Me, MeO, Cl, or EtO; n = 1 or 2; X = $(CH_2)_n$ or O; X^1 = NHC(Z)NH; Z = O or S.

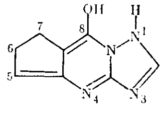


(XCVI)



(XCVII)

Polymers containing the 1,2,4-triazolo[1,3-*a*]pyrimidinyl group have been patented as stabilisers of photographic silver halide materials:[185]



The most promising trend in this field comprises studies on the biological activity and photochemical properties of compounds of the class considered.

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Studies of Polyacetylene by Magnetic Resonance Methods

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Results obtained in studies of polyacetylene (PA) by magnetic resonance methods are discussed. The structure and properties of the paramagnetic centres in PA are examined, and compared with the structure and the chemical composition of pure and of doped PA (i.e. PA with added electron donors and acceptors).
The bibliography includes 116 references.

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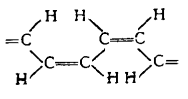
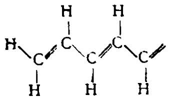
I. INTRODUCTION

In recent years polyacetylene (PA) has attracted much scientific interest because of its unusual electrical properties. An increase in electrical conductivity by 10–12 orders of magnitude has been obtained by adding donor or acceptor impurities (see Ref.1), equivalent to the transition from a dielectric to an "organic metal" with a conductivity $\sigma \cong 10^3\ \Omega^{-1}\ cm^{-1}$. In chemical composition polyacetylene $(CH)_x$ is the simplest of all the polymers with conjugated double bonds, whose conductivity is determined by the presence of impurities; therefore PA has been repeatedly chosen as a model system for studies of this unusual phenomenon. The properties observed in these studies appear to be general, and present in many other conjugated systems. Therefore the conclusions and hypotheses formulated from studies of the properties of PA may be equally applicable to other polymers with conjugated bonds. However, though PA is still the subject of most of the publications on polymers with conjugated bonds, papers on other similar systems have recently started to appear (polyphenylene and its derivatives, polypyrrole, etc.). These studies lack both the generality and the fullness of the work on PA, and in particular they do not provide a complete picture of the physical, chemical, and physicochemical changes resulting from the addition of impurities. Additional interest in the study of polymers with conjugated bonds has recently been stimulated by the development of effective methods of synthesis which allow the production of polymers with reproducible physicochemical properties.

We know[2–4] that the structure of PA consists of polymer chains in the *cis* or the *trans* form,



cis form



trans form

arranged in parallel bundles to form a fibre (or fibril) a few hundreds of Ångstroms thick and several thousands long. The long axes of these fibrils are randomly arranged, but they can be partially oriented by stretching the sample. Within each fibril the polymer chains are close-packed, and form a crystalline structure.[2,3] Thus PA is an unusual type of polycrystalline material, consisting of "crystalline fibrils".

This review discusses the properties of PA prepared by Shirakawa's method,[4] in which a stream of gaseous acetylene is directed at a thin layer of solution containing a Ziegler–Natta catalyst at 195 K. This produces a thin layer of polymeric material with a fibrillar structure. There are alternative methods of preparing PA, for example by first preparing an easily soluble polymer precursor and then heating it to give insoluble PA.[5,6] This material contains few defects, and is largely amorphous. However, most of the published work was done with PA prepared by Shirakawa's method.[4]

The fibrillar structure of PA facilitates its "doping", carried out as follows. The chemical additives ("dopants"), for example the electron-acceptor impurities I_2 or AsF_5, penetrate into the PA fibrils through their surface and interact with the polymer chains or among themselves. The result is the formation of the I_3^- or AsF_6^- anions, while part of the PA chain acquires a positive charge. Thus the addition of chemical impurities is only the first step in the doping of PA: the process includes several chemical changes and is completed by the partial conversion of the PA into an ion-radical salt containing charge transfer complexes.

Both doped and undoped PA have been extensively studied by magnetic resonance methods: ESR, NMR, electron–nucleus double resonance (ENDOR), dynamic nuclear polarisation (DNP), nuclear quadrupole resonance (NQR), and their time-resolved modifications. These methods offer varied and unique information on the structure of the polymer (bond length, size of conjugation regions, etc.), on the nature and properties of the paramagnetic centres, on the extent and nature of the doping, and on the distribution of charge and spin density in the polymer chains of undoped and of doped PA. This paper reviews the experimental studies of the structure and properties of PA by magnetic resonance methods. The theoretical foundations of the magnetic resonance methods and the apparatus used in this work are discussed in several monographs,[7–17] and will not be the object of this review. A generally accepted model of the paramagnetic centre in PA has not yet been proposed, and as a result we still lack a unique terminology. In the present review we shall use general terms such as "paramagnetic defect", "unpaired electron", etc., avoiding as far as possible the term "soliton" applied by some workers to a particular model of defects in PA.

II. PARAMAGNETIC SUSCEPTIBILITY OF PURE PA

Like most conjugated systems, polyacetylene shows paramagnetism. This has been reliably established by studies of its static magnetic susceptibility (Faraday's method)[11] and by ESR measurements.[8,10,11] The paramagnetic susceptibility of *trans*-PA at room temperature is an order of magnitude greater than that of the *cis* isomer, and is equivalent on average to one paramagnetic centre per ~3000 CH units.[1,4,18–25] The molecular weight of the polymer is ~7000, i.e. the chains consist of approximately 400–500 CH units.[26] Obviously, this number depends on the method of synthesis of the PA. However, on average one paramagnetic centre is shared by 6–7 polymer chains.

In the ESR spectra of the *cis* and *trans* PA isomers we find a singlet line[19] with a *g* factor of 2.003, but in the *cis* isomer synthesised at 195 K the ESR signal with $g = 2.003$ is absent.[24,25,27,28] The signal appears only on raising the temperature, and at 300 K the concentration of paramagnetic centres reaches 10^{18} spins g^{-1} (i.e. one spin per 44 000 CH units). If the *cis* isomer at 77 K is irradiated with u.v. light[28] or treated with oxygen[24,25] it develops the same ESR signal as if the temperature is increased. On the other hand if a sample heated to room temperature is exposed to oxygen the amplitude of the ESR signal increases by almost an order of magnitude, and the width of the line (~8 Oe) stays almost unchanged.[24,25,27] The effect of u.v. irradiation and of oxygen on the *trans* isomer differs slightly from their effect on the *cis* isomer. The ESR signal is not increased by u.v. irradiation of the *trans* isomer. On exposure of this isomer to oxygen the signal initially increases, and then decreases,[24,29,30] while the width of the ESR line increases.[24,29]

Heating PA to 423 K produces a large increase in the number of paramagnetic centres according to the ESR results.[21,27,29] We know[31] that at 418 K an exothermic peak (attributed to *cis–trans* isomerisation) appears in the thermogram of polyacetylene. Heating of *cis*-PA produces two effects: *cis–trans* isomerisation and polymer degradation. It was reported[32] that the optimum region for the preparation of *trans*-PA is 413–423 K, because at these temperatures the rate of isomerisation is a maximum while the rate of degradation is still acceptably low.

It has been suggested[4] that the paramagnetism of PA is caused by the presence of defects: *cis*-PA has a more perfect structure, and it contains fewer defects than *trans*-PA. *Cis–trans* isomerisation results in an increase in the defect density of the polymer, accompanied by a corresponding increase in the absolute value of the paramagnetic susceptibility. Similar views are expressed in more recent papers (see, for example, Refs.21 and 27). The ESR signal observed in *cis*-PA at room temperature has been attributed[22,24] to the presence of ~5% of *trans*-PA in the sample. It was suggested that fragments of the *trans* isomer are localised at the ends of the polymer chain, where *cis–trans* isomerisation occurs most readily. Noting the similarity (Fig.1) between the temperature dependences of the concentration of *trans* isomers (obtained from the i.r. spectra) and of free radicals Zanobi and D'Ilario[28] suggested that isomerisation causes breaking of the double bonds with formation of regions containing an odd number of π electrons.

A simple model of a defect in *trans*-PA is the formation of a cross-link between chains.[33] Cross-linking produces a fragment with an odd number of carbon atoms, which contains an unpaired electron. The model in which defects are identified with cross-links is discussed in Ref.34. After the cross-link is established one radical appears in each chain: the energy of this biradical state was calculated by the quantum-chemical INDO method. Other workers[27–29] have expressed similar views on the causes of the effect of oxygen on the ESR signal in PA. Oxygen catalyses the *cis–trans* isomerisation process in PA and initiates the chemical oxidation of PA, i.e. it acts as a dopant of the acceptor type. At the same time the oxygen takes part in chemical reactions with the PA which result in degradation of the latter.

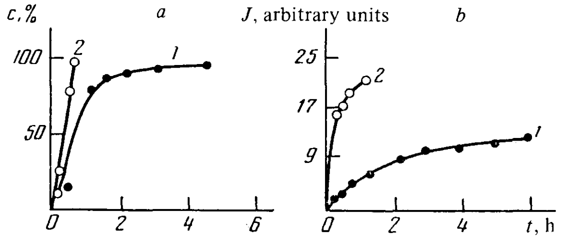


Figure 1. Kinetics of the change in the concentration of the *trans* isomer of PA (from i.r. data) (*a*) and in the concentration *J* of free radicals in PA (from ESR data) (*b*) as a function of the hold time *t* of the sample at 383 K (*1*) and 493 K (*2*) (from Ref.28).

No detailed studies of the effect of oxygen on the structure and properties of PA have yet been reported. Most workers give only a qualitative estimate of the effect of oxygen on their measurements (for example, they quote the dependence of a measured parameter on the time of exposure of the sample to air or to an oxygen atmosphere). However, oxygen has a marked effect on the paramagnetism of PA, as was clearly shown by Bernier and co-workers:[27] in the absence of oxygen these workers observed in *cis*-PA a broad signal from a catalyst present at a concentration of 0.2% of the number of CH groups, but after contact with oxygen this signal was completely suppressed, and was replaced by a narrow ESR signal of increasing intensity which was attributed to *trans*-PA.

Studies of the paramagnetic susceptibility χ of the *trans* isomer at 0.03–300 K have revealed the presence of Curie paramagnetism: the magnetic susceptibility χ_c is proportional to $1/T$.[4,16–18,35–41] Curie paramagnetism has also been observed[4,22,23] in *cis*-PA at 2–295 K. However, according to Tomkiewicz and co-workers[18] the magnetic susceptibility of the *cis* isomer is not described by Curie's law at 4–300 K. The reason for these discrepancies is not clear.

III. TYPES OF PARAMAGNETIC DEFECT IN PURE PA

All the experimental results obtained by ESR, ENDOR, and NMR methods indicate the presence of an unpaired electron in the π system. Careful measurements of the *g*-factor in undoped PA, and also in the *cis* and *trans* isomers doped with AsF_5, showed[19] that in every case

$g = 2.002634 \pm 0.000015$, which is much higher than the g-factor for the free electron (2.0023). These high values of the g-factor are characteristic of an unpaired electron in a π system.[10,11]

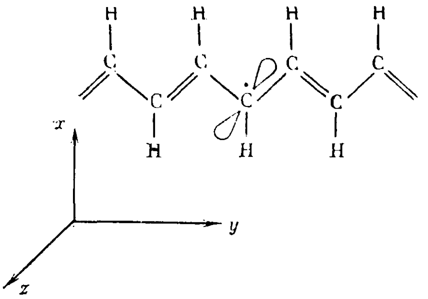


Figure 2. Orientation of the polymer axis with respect to the 2p π orbital of the paramagnetic defect in *trans*-PA.

In an ideal stretched film of $(CH)_x$ all the fibril axes (y) and therefore also the axes of the polymer molecules are oriented in the stretching direction. Partial orientation of the fibrils can be obtained by stretching the sample (film) in a particular direction.[42] The appearance of g-factor anisotropy in such a film can be explained in terms of the nature of the 2p π orbital of the paramagnetic defect (see Fig.2): the unpaired π electrons occupy atomic orbitals perpendicular to the y axis (the fibril axis). ESR measurements[43] in the millimetric region gave very precise values of the g-tensor for the *cis* and *trans* isomers in oriented and in non-oriented samples at temperatures in the range 4.2–300 K. For *cis*-PA they found $g_{\|} = 2.004$ and $g_{\perp} = 2.003$ {where $g_{\|}$ and $g_{\perp}$ are for magnetic fields parallel and perpendicular (respectively) to the axis of the polymer chain}. These values of the g-tensor components agree with published data.[44]

The components of the g-tensor have also been calculated[43] by a special variant of the molecular orbital method[45] for *cis* and *trans* $(CH)_n$ fragments where n is an odd number between 5 and 15. In chains with $n \geqq 9$ the g-factor has become independent of n, and can therefore be interpreted as the g-factor for a long fragment. The calculations were made for structures with C–C bonds of equal length and for structures with alternating double and single bonds. The g-tensors calculated for these two types of structure (with $n \geqq 9$) were equal to the experimental values: according to the calculation $g_{\|} = 2.0034$ and $g_{\perp} = 2.0028$. The g-factor anisotropy ($|\Delta g| = |g_{\|} - g_{\perp}|$) for the 2$p$ π electron in small molecules with conjugated bonds is usually 0.001–0.002.[46] The smaller value of this difference observed experimentally[43,44] can be attributed to a lower level of orientation of the polymer chains.

The components of the hyperfine interaction (HFI) tensor of the electron with the protons and the ^{13}C nuclei for *cis*-PA (with a 99% enrichment in ^{13}C) have been determined[43,47–49] by the ENDOR method (see Section IV). The symmetry of the tensors and the relative values of the isotropic and the anisotropic components suggest that the unpaired electron occupies a π orbital. This conclusion is confirmed by an ENDOR study[50] at 77 K of *cis*-PA films in which the polymer chains had been oriented by stretching the sample.

The presence of an unpaired electron in the π system is observed also in the NMR spectra, because local electronic configurations produce local anisotropic fields which interact with the magnetic nuclei. The high-resolution NMR technique has been used[51] to determine the diagonal elements of the chemical shift tensor (σ_{11}, σ_{22}, σ_{33}) on ^{13}C for the *cis* and *trans* isomers. Both isomers gave values of the tensor components typical of conjugated systems.

A study[52,53] of a mixture of PA isomers and of the pure *trans*-PA isomer by the electron spin echo (ESE) method showed that localised defects (possibly consisting of σ radicals) are present in PA in addition to the delocalised π defects. The concentration of localised defects is approximately 100 times lower than the concentration of delocalised defects, and therefore the magnetic behaviour of the system as a whole is determined mainly by the π defects.

IV. DELOCALISATION REGION OF THE UNPAIRED ELECTRON AND SPIN DENSITIES IN PURE PA

Table 1. Components of the HFI tensor (in MHz) for ^1H and ^{13}C (99% enrichment) in *cis*-PA, calculated from measurements at 136 K (Ref.47).

Index	^1H			^{13}C		
	A_x	A_y	A_z	A_x	A_y	A_z
1	−0.5	−2.1	−1.1	−1.3	−1.3	−2.1
2	−1.8	−7.0	−3.9	−3.1	−3.1	7.0

Detailed studies of spin densities in solids are usually made by the ENDOR method. Table 1 shows the components of the HFI tensors obtained[43,47–49,54] from the characteristic ENDOR frequencies of *cis*-PA 99% enriched in ^{13}C. The experimental ENDOR spectrum for ^1H and ^{13}C is described by two pairs of tensors (of index 1 and 2) corresponding to the two types of carbon and hydrogen atom. The HFI tensor components given in Table 1 were obtained by numerical modelling of the experimental spectrum allowing for all the interactions of the electronic and nuclear spins in all the magnetic fields present in the system and using the appropriate relaxation times. As Table 1 shows, the HFI tensor for ^{13}C is characterised by an axial symmetry and small values of the isotropic HFI constants, typical of defects in the π system. The symmetry and the relative values of the diagonal elements of the tensor for the HFI with the ^1H nuclei are the same as for the α protons.[13] Thus both the symmetry and the value of the tensor elements for ^{13}C and for ^1H unambiguously indicate the presence of a paramagnetic defect (unpaired spin) on a π orbital and the existence of two types of carbon atom with an unpaired electron.

The following spin densities of the unpaired electron on carbon were calculated from the HFI tensors for ^{13}C (Table 1): $|\rho(C_1)| = 0.06$ and $|\rho(C_2)| = 0.02$.[47] Studies by triple electron–electron resonance[47] showed that the spin densities on these two types of carbon atoms have different signs: $\rho(C_1)$ is positive and $\rho(C_2)$ is negative, and these densities are alternating along the polymer chain. The signs and amplitudes of the spin densities suggest a substantial delocalisation of the π orbital on a region of the chain approximately 47 CH units long (i.e. ~100 Å). An estimate of the total number of atoms ($2n + 1 \cong 47$) in the paramagnetic fragment is obtained from the condition $n\rho(C_2) + (n + 1)\rho(C_1) = 1$.[43] The interaction of the paramagnetic defect with the protons in 70% *cis*-PA is also thought[55] to be characterised by two sets of HFI parameters, corresponding to two values of the spin density on the carbon atoms differing in magnitude and in sign. In 70% *cis*-PA the delocalisation region of the unpaired electron was calculated[55] to be 93 CH units, i.e. double the value given in Refs. 43 and 47.

The spin density has been calculated[43] by the methods of Hückel and McLachlan (of which the latter gives a negative spin density in π radicals) for $(CH)_n$ fragments with odd values of n between 3 and 99. Two types of structure were considered: with bonds of equal length and with alternating bond lengths. The latter model of the $(CH)_n$ fragments gave a qualitative agreement with experiment: an alternation of the signs along the chain, but the absolute density values show a large scatter which should prevent the formation of a resolved ENDOR spectrum (though such a spectrum is observed experimentally). The hypothesis of uniform bond lengths in $(CH)_n$ fragments with odd values of n has not so far been tested by any other method. Since the total number of carbon atoms associated with one spin in *trans*-PA is ~3000,[22] the 47 carbon atoms in the fragment with an unpaired electron and equal bond lengths accounts for only 1.6% of the total number of carbon atoms in the sample.[43] A calculation[50] of the frequencies of the ENDOR spectrum using the spin densities specified by the soliton theory[56,57] gave the best agreement with experiment when the corrections for negative spin densities were used. However, no definite conclusion as to the distribution of spin densities could be reached[50] from the ENDOR spectra obtained in this work.

The ENDOR spectrum of *trans*-PA is reported[55,58] to be singlet. The delocalisation of the paramagnetic defect in *trans*-PA is thought[55] to be very extensive, i.e. each carbon atom in the delocalisation region carries only a small fraction of the spin density. Therefore the hyperfine structure (HFS) is unresolved even when the ENDOR method is used.

V. VIEWS ON THE MOTION OF A PARAMAGNETIC DEFECT IN PA

The DNP method[12] has been widely used in studies of the static and dynamic characteristics of unpaired electrons in solids. It was first applied to the study of paramagnetic defects in PA by observing the NMR proton signal[59-61] in a saturated u.h.f. transition at a frequency close to the ESR resonance frequency (ν_e = 8190 MHz). Two extreme cases are possible, depending on whether the electron–nucleus interaction is static or dynamic.[9] For a static interaction the unpaired electrons are "fixed" in space (at least, their jumping frequency is smaller than the NMR frequency, ν_n), and forbidden transitions at the frequency $\nu_e \pm \nu_n$ are induced by the electromagnetic field. This is the so-called solid effect. On the other hand if the unpaired electrons are mobile (on the time scale of the frequency ν_e) the intensity of the NMR signal may be increased at the frequency ν_n (the Overhauser effect). In pure *trans*-PA at 300 K a single Overhauser effect was observed,[61] whereas a mixture of the *cis* and *trans* isomers gave a superposition of the Overhauser effect and of the solid effect. In the mixed samples the proportion of the Overhauser effect increases with the content of the *trans* isomer (see Fig. 3). In Ref. 62 the same signal is obtained as in Ref. 61 for the mixture of isomers, but a weak solid effect is reported, in addition to the Overhauser effect, for the pure *trans*-PA. This discrepancy may be due to an impurity of the *cis* isomer in the latter case.[62] The following conclusions were formulated from the results of Ref. 61: 1) in the *trans* isomer the unpaired electrons are mobile, and the lower limit of their diffusion rate is ~5 × 10^{10} rad s^{-1} (determined from the ESR working frequency ν_e); 2) in *cis*-PA the unpaired electrons are fixed; 3) during the *cis*–*trans* isomerisation some previously fixed unpaired electrons become mobile.

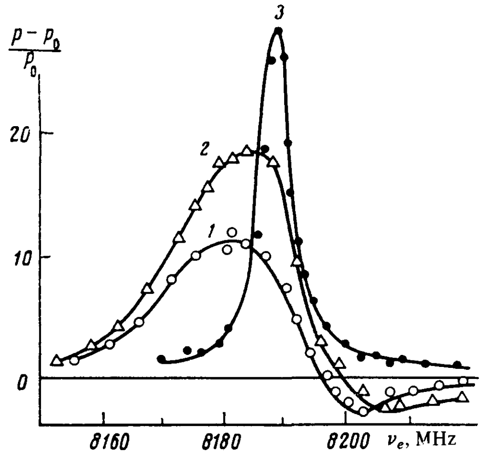


Figure 3. Increase in the amplitude of the ^{1}H NMR signal at different frequencies ν_e of the saturating field for concentrations of the *trans* phase in undoped PA of 50 (*1*), 65 (*2*), and 100% (*3*); T = 300 K (P_0 and P are the NMR signals without microwave saturation and with saturation respectively).

On cooling *trans*-PA we produce a change in the DNP signal: the characteristic signal of the pure Oberhauser effect (observed at room temperature) is replaced at 5.5 K by a signal corresponding to the solid effect.[63,64] The electrons which are mobile at high temperatures are slowed down, and their characteristic frequency, inversely proportional to the time of residence of the unpaired electron near the nucleus (i.e. the characteristic velocity of the electron), becomes smaller than the NMR frequency (10^7 s^{-1}). A smooth change from the Oberhauser effect to the solid effect has been observed[65] during temperature changes from 300 to 4 K (the two effects being comparable at 40–50 K). The exposure of *trans*-PA to oxygen produces the same effect as cooling the sample:[60] the presence of O_2 "freezes" the motion of the unpaired electron. The superposition of the signals corresponding to the Oberhauser effect and to the salt effect in the presence of air has been observed previously in other conjugated polymers.[66]

The study of the components of the g-tensor (ESR in the millimetre band) and of the HFI tensors (ENDOR spectra) for PA at 4–300 K led to the conclusion[43,47] that the paramagnetic centres are mobile in the *trans* isomer and fixed in the *cis* isomer. The presence of mobile paramagnetic centres in *trans*-PA is indicated also by ESE measurements on protonated and deuteriated samples at 4–300 K.[51-53,67,68] Masin and co-workers[69] concluded from the kinetics of the damping of the NMR signal of ^{13}C that unpaired electrons are not generally found in PA. However, it has been pointed out[70] that this conclusion may be valid only for the particular samples studied in that work.[69]

VI. QUANTITATIVE CHARACTERISTICS OF A MOBILE PARAMAGNETIC DEFECT

The motion of the paramagnetic centre in PA is usually described in terms of the measured nuclear (T_{1n}) and electronic (T_{1e}) relaxation times by using formulae for two models of the motion: one-dimensional diffusion of the paramagnetic centre along the polymer chain and three-dimensional diffusion of the nuclear spin polarisation towards a fixed paramagnetic centre. For the first model of the motion a theoretical expression which had been previously applied in studies of the conducting tetracyanoquinodimethane (TCNQM)[61] has been proposed:[71-73]

$$T_1^{-1}(n) = kT\chi\left[\frac{3}{5}d^2 f(\omega_n) + \left(a^2 + \frac{7}{5}d^2\right) f(\omega_e)\right] \qquad (1)$$

Here χ is the normalised spin susceptibility ($\chi = \chi_{mol}/\nu(g\mu_B)^2$, where ν is the concentration of paramagnetic centres); a and d are the constants for the isotropic and the dipolar electron–proton interaction respectively; $f(\omega)$ is the spectral density function; ω_n and ω_e are the Larmor frequencies of the nuclear and the electron spin respectively; μ_B is the Bohr magneton.

Eqn.(1) is valid when the electronic and the nuclear Zeeman energies are much less than kT, i.e. at relatively high temperatures ($T > 4$ K). For the one-dimensional diffusion of the paramagnetic centre, allowing for the HFI, the function $f(\omega)$ takes the form[74]

$$f(\omega) = \frac{1}{(2W_\parallel\omega)^{1/2}} - C_L;\ C_L \approx 0{,}37\frac{L}{W_\parallel} \qquad (2)$$

where $W_\parallel$ is the diffusion rate of the electron along the chain, and L is the size of the delocalisation region.

The quantity $W_\parallel$ is related to the diffusion constant $D_\parallel$ by the expression

$$W_\parallel = D_\parallel b^{-2}$$

where b is the distance between the CH fragments along the chain of *trans*-PA ($b = 2.46$ Å). At low frequencies the one-dimensional diffusion can be perturbed by inter-chain jumps, so that the system behaves as two- or three-dimensional. The transition from one-dimensional to two- or three-dimensional motion occurs at the frequency $\omega_c = W_\perp$, where $W_\perp$ is the rate of inter-chain diffusion.

In the model which assumes diffusion of the polarisation of the nuclear spin towards a fixed paramagnetic centre the expression for $T_1^{-1}(n)$ is[9]

$$T_1^{-1}(n) = \frac{4}{3}\pi\rho T_{1e}^{-1/4}(\mu_B/\gamma_n)^{1/4}\bar{D}^{3/4}\omega_n^{-1/2} \qquad (3)$$

where $\bar{D}$ is the diffusion constant of the polarisation of nuclear spins and ρ is the electronic spin density.

It follows from the usual model[9] of the diffusion of nuclear spin polarisation that $T_1^{-1}(n)$ is independent of the magnetic field strength at a frequency below the value for which $\tau_c < \omega_n^{-1}$, where τ_c is the characteristic damping time of the z-component of the magnetisation of the unpaired electron (assuming an exponential decay), located in the vicinity of a relaxing nucleus. The quantity τ_c is determined by the electronic relaxation time T_{1e} or by the electronic "flip–flop" transition time (more accurately, by the shorter of these two times). Under these conditions $T_1^{-1}(n)$ should be independent of temperature in the region of weak magnetic fields.

Since all the quantities which appear in formulae (1) and (3) are experimentally known we can determing $\bar{D}$ or $W_\parallel$ by measuring $T_1^{-1}(n)$. This determination of the diffusion coefficients of the electronic or the nuclear polarisation becomes incorrect if the system of nuclear spins cannot be characterised by a single spin temperature. Experimental dependences of T_1^{-1}(H) on ω_n at different temperatures have been obtained[61,66,71,75,76] for the protons of *trans*-PA. As Fig.4 shows, the dependence of T_1^{-1}(H) on $\omega_n^{-1/2}$ is linear in the experimental temperature range 0.45–295 K, and the straight line for room temperature passes through the origin whereas the lines for lower temperatures give a finite intercept ($\sim C_L$) on the horizontal axis.[75] Various workers[60,61,66,71,75,77,78] have explained the experimentally observed dependences of T_1^{-1}(H) on T and ω_n by postulating one-dimensional diffusion of the unpaired electron. Some believe[71,75] that even at 4 K 1.5% of the paramagnetic centres are mobile. Values of $W_\parallel = 4 \times 10^{13}$ rad s^{-1} and $D_\parallel = 4 \times 10^{-3}$ cm^2 s^{-1} were calculated[71] for 300 K. This value of the D diffusion coefficient is too high for a dielectric such as polyacetylene, and comparable with the D value for the metallic TCNQM salts.[72]

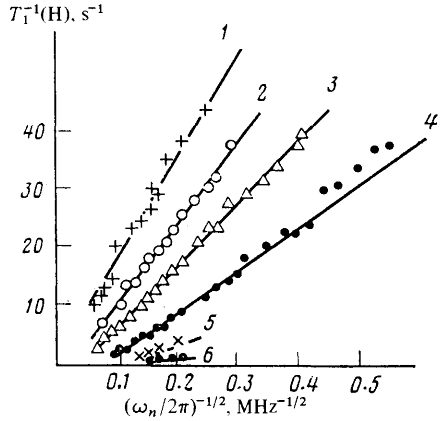


Figure 4. Rate of proton relaxation $T^{-1}(H)$ in *trans*-PA against $\omega_n^{-1/2}$ at 295 (*1*), 77 (*2*), 30 (*3*), 4.2 (*4*), 1 (*5*), and 0.45 K (*6*) (Ref.75).

The $W_\parallel$ value obtained from the ESE spectra[67,68,79] was three orders of magnitude lower than the above. The reason for this discrepancy is not clear, but a likely explanation is inadequacy of the chosen diffusion model. The $W_\parallel(T)$ dependence has been determined[71,75] from experimental data on the dependence of T_1^{-1}(H) on ω_n at different temperatures and on the dependence of the width of the ESR line (ΔH) on T. A similar $W_\parallel(T)$ dependence, i.e. an increase in $W_\parallel$ with T, was obtained from an analysis of the ESE spectra.[67,68,79]

The results of a study of the effect on $T_1^{-1}(n)$ of the isotopic replacement of hydrogen by deuterium[65] at 4.2 K were interpreted[65] by the model of the diffusion of nuclear spin polarisation towards a fixed unpaired electron. The calculated[65] threshold value of the magnetic field for which the $T_1^{-1}(n) \propto \omega^{-1/2}$ dependence (characteristic of one-dimensional diffusion) ceases to apply and the $T_1^{-1}(n)$ dependence becomes independent of the magnetic field is ~3 Oe, which is acceptably close to the experimental value (20 Oe). More recent results obtained[80] with *trans*-PA films (deuteriated, and enriched in ^{13}C) at room temperature are shown in Table 2. The $T_1^{-1}(n)$ values were measured on three samples containing different amounts of ^1H and ^{13}C. We can see from the Table that in the sample with a high concentration of magnetic nuclei $T_1^{-1}(H)$ exceeds $T_1^{-1}(^{13}C)$ by more than an order of magnitude. A similar result is reported in Ref.81, with $T_1^{-1}(H) \propto \omega^{-1/2}$, whereas $T_1^{-1}(^{13}C)$ is independent of frequency. The ^{13}C nuclei (in contrast to the ^1H and ^2H nuclei) show a non-exponential decay: the extent of damping varies with t approximately by a $t^{1/2}$ law. It was found[72] that the ^{13}C nucleus relaxes with two characteristic times (0.3 and 1.5 s), so that we should consider two different velocities: $T_1^{-1}(^{13}C) \cong 3\ s^{-1}$ and $T_1^{-1}(^{13}C) \cong 0.7\ s^{-1}$. Therefore the $T_1^{-1}(^{13}C)$ values given in Table 2 should be interpreted at best as the average of two velocities.

Table 2. Values of $T_1^{-1}(n)$ for three samples of *trans*-PA of different isotopic composition.

Sample	Isotope concentrations		ν, MHz	$T_1^{-1}(H)$, s^{-1}	$T_1^{-1}(^{13}C)$, s^{-1}
	$[^1H]$, %	$[^{13}C]$, %			
1	100	98	90	18±1	—
1	100	98	23	37.3±2	1.9±0.1
1	100	98	11.5	45±3	1.9±0.1
2	2	90	23	—	2.6±0.2
2	2	90	12	—	2.6±0.1
3	2	20	12	—	0.9±0.2
3	2	20	23	—	0.9±0.2

In planning the experiment with samples enriched in ^{13}C it was assumed[80] that $T_1^{-1}(H)$ and $T_1^{-1}(^{13}C)$ would have the same frequency dependence and absolute value, since the HFI constants of the unpaired electron in ^1H and ^{13}C are similar.[10,48,49,68] The assumption is valid if all the nuclear relaxation processes are determined exclusively by interactions with a mobile unpaired electron. From the lack of frequency dependence of $T_1^{-1}(^{13}C)$ (see Table 2) it follows that the results of the ^{13}C are not correctly described by the models which assume diffusion of the polarisation of electrons or nuclei. The following qualitative model of the relaxation for isotopic nuclei in the polymer chain was proposed.[80] In the case of nuclei in a polymer fragment containing a mobile paramagnetic defect the main relaxation channel is the HFI. Equilibrium between these nuclei and the others is reached as a result of the diffusion of nuclear spin polarisation: in other words, according to this model the system of nuclear spins cannot be characterised by a single spin temperature. Obviously, for a quantitative description of the experiments with ^{13}C further theoretical development of the unpaired electron diffusion model is required.† It has been suggested[65] that the views expressed in Ref.80 are the most likely to lead to a convincing explanation of the increasing volume of experimental $T_1^{-1}(n)$ data.

The rate of electronic spin–lattice relaxation T_{1e}^{-1} has been studied[84] in *trans*-PA in the frequency range 5–450 MHz at room temperature. For protonated and deuteriated samples the T_{1e}^{-1} values at frequencies ≥ 20 MHz are accurately described by the $T_{1e}^{-1} \propto \omega^{-1/2}$ relationship, previously established for the rates of proton relaxation.[61,66,71,75,76] The same relationship was obtained by other workers[68,82,83] at higher frequencies (9–17 GHz). At a frequency of ~20 MHz (with a field of ~6 Oe) a deviation from this relationship was observed,[84] and at frequencies < 10 MHz T_{1e}^{-1} was independent of frequency. The T_{1e}^{-1} values for deuteriated PA samples are somewhat lower (by ~50%) than the values for the protonated samples. The observed $T_{1e}^{-1}(\omega)$ frequency dependence was ascribed[84] to the one-dimensional diffusion of the unpaired electron along the polymer chain, and the frequency 10 MHz (3 Oe) was assigned to the inter-chain jumps.

As was stated above, the measurement of $T_1^{-1}(H)$ suggested that the diffusion ceases to be one-dimensional at a field strength of ~20 Oe, which is close to the value inferred from T_{1e}^{-1} data. A study[84] of the dependence of T_{1e}^{-1} on the concentration of paramagnetic centres in PA showed that the T_{1e}^{-1} value is determined by the dipole and hyperfine interactions of the unpaired electron with the protons. The coefficients and rate constants for diffusion of the unpaired electron were also determined,[84] and found to be close to the values determined[60,61,71] from measurements of $T_1^{-1}(H)$. We should stress that the interpretation of the T_{1e}^{-1} data is more unambiguous than the interpretation of the $T_1^{-1}(n)$ data, since the relaxation rate T_{1e}^{-1} is associated only with the diffusion of the unpaired electron.

The addition of dopants (Br_2, I_2, AsF_5) to PA has no effect[61,77,78] on the frequency dependence of the rate of proton relaxation $T_1^{-1}(H) \propto \omega_n^{-1/2}$, but it makes the relaxation rates $T_1^{-1}(H)$ and $T_1^{-1}(^{13}C)$ lower than in the pure PA.[1,67,69,77,78,85] The most marked decrease in these quantities is found by using AsF_5; I_2 and Br_2 have similar effects, almost an order of magnitude lower than that of AsF_5. The value $W_{\parallel} = 1.7 \times 10^{17}$ rad s^{-1} has been calculated[61] for PA doped with AsF_5: this is 10^3 times higher than the analogous value for undoped PA. The anisotropy ($W_{\parallel}/W_{\perp}$) is also not very different from that of the undoped polymer, i.e. ~10^6.

VII. PROPERTIES OF THE PARAMAGNETIC CENTRES IN PURE PA INFERRED FROM THE SHAPE OF THE ESR LINE

The shape of the ESR line depends on the properties of the paramagnetic centres in PA, but its analysis yields little quantitative information.# Early studies of the application of ESR to PA are mainly of historical interest, due to the fact that they stimulated the application of more advanced methods to the study of PA (ESE, ENDOR, and DNP).

The ESR signal in *cis* and *trans* PA is a singlet with $g = 2.0036$ (the measurements of the g-factor and g-tensor are discussed in Section III). Large differences are found between the determinations of the line width (ΔH) by various workers: from 7 to 9.5 Oe for the *cis* isomer[4,23,24,28,5] and from 0.28 to 5 Oe for the *trans* isomer,[60] i.e. the largest scatter occurs in the ΔH values for *trans*-PA. This is

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†A further theoretical development of this model has appeared in a paper by P.K.Kahol, M.Mehring, and X.Wu (J.Phys.(Paris), 1985, v.46, p.1683).

#The same view is expressed in the theoretical paper by P.K.Kahol and M.Mehring (J.Phys.C, Solid State Phys., 1986, v.19, p.1045), whose aim was to demonstrate the unsuitability of the ESR method for determining spin densities and the delocalisation region of the unpaired electron from an analysis of the shape of the ESR line.

apparently due to differences in the preparative techniques used by different workers, since the parameter ΔH depends on the duration and temperature of the *cis–trans* isomerisation process, on the presence of oxygen, etc.

A special study[60] of the scatter in the measured values of ΔH suggested that the presence of uncontrolled amounts of oxygen is the main reason for the disagreement between the results of different workers. The smallest width of the ESR line obtained[60] by the meticulous application of all possible measures to prevent the access of oxygen to the system during all stages of the sample preparation and of the measurements was 0.44 Oe. This value is slightly higher than the value $\Delta H = 0.28$ Oe given in Ref.86. The line width $\Delta H = 1$ Oe in the spectrum of *trans*-PA is attributed[60] to the presence of 50 p.p.m. of oxygen. Special protective measures are needed to eliminate these very small contaminations.

The change from protonated to deuteriated PA produced a substantial narrowing of the ESR signal,[21,22,40] but a broadening of the ESR line was also reported[24] following the enrichment of *cis* and *trans* isomer samples with ^{13}C. The inconsistent changes in ΔH caused by isotopic replacement are due to differences in the magnetic moments of the nuclei ^{1}H, ^{2}H, and ^{13}C, and suggest the presence of an unresolved HFS. The absence of a resolved HFS in PA was initially attributed to exchange narrowing of the signal (see, for example, Refs.18, 19, 29, and 40). However, this work revealed a strong dependence of ΔH on T, which would not be expected for line narrowing by the exchange mechanism.[22,24,40,87] Fast one-dimensional motion of the paramagnetic centres has been suggested[22,40,60,63,87] as the reason for the narrowing of the ESR line.

The ESR line for *cis*-PA is Gaussian.[1] For the *trans* isomer in the temperature range 0–296 K a Lorentzian line, characteristic of exchange interaction, has been observed.[19] A Lorentzian line was reported[87] even when the temperature was lowered to 2 K, but deviations from this form were later observed. There have been attempts[22,56,60,63] to model the experimental spectrum by allowing for dipole–dipole and hyperfine interactions, repulsion between the electrons, and the one-dimensional diffusion of the unpaired electron along the chain. The model proposed in Ref.60 gives the best description of the experimental results. An analysis of the experimental line by this model showed[60,63] that the shape of the ESR line is different in different samples, and that it depends on temperature and on the presence of oxygen. In other words, it was made clear that the shape of the ESR line is not a fundamental property of PA itself. The width of the ESR line was not calculated exactly,[60] but the broadening due to the motion of the unpaired electron ($\Delta H = 0.15$ Oe) was estimated, and used to calculate the rate of diffusion along the chain $W_{\|} = 8 \times 10^{12}$–$8 \times 10^{13}$ rad s^{-1}. This value of $W_{\|}$ agrees well with the value deduced from measurements of $T_1^{-1}(\mathrm{H})$ (6×10^{13} rad s^{-1}).[59]

This work[60] is the only reported instance of consistent diffusion rates $W_{\|}$ obtained from ESR and NMR measurements. The $W_{\|}$ values obtained by the two methods usually differ by a factor of 10–10^3.[60,88] According to calculations[22] based on an analysis of the ESR line shape ($\Delta H = 4$ Oe) the delocalisation region of the paramagnetic centre in *cis*-PA is ~14 CH units. For *trans*-PA a calculation of the second component M_{2e} of the ESR line[71] gives a delocalisation region of ~10 CH units for the soliton model of the distribution of spin density[56,89] or ~7 CH units if the spin density is assumed to be constant within the delocalisation region. However, by using the ENDOR values[43] of the spin density (see Section IV), which correspond to a delocalisation length of ~50 CH units, we again obtain good agreement between experiment and calculation for M_{2e} in protonated and in fully deuteriated PA. The calculation of the difference ΔM_{2e} by the formula[71]

$$\Delta M_{2e} = M_{2e} - M_{2e}^{*} = 140\Sigma\rho_i^2 \qquad (4)$$

where M_{2e} and M_{2e}^{*} are the second components of the ESR line for protonated and for deuteriated PA respectively, gives similar values for substantially different distributions of the spin density. Thus, $\Delta M_{2e} = 20$ Oe^2 for a constant ρ_i over a fragment 7 CH units long and $\Delta M_{2e} = 14$ Oe^2 for the model in which ρ_i is distributed (with a sign alternation) over 47 CH units.[43] The experimental value of ΔM_{2e} is 20 ± 4 Oe^2.[80]

VIII. CHARACTERISTICS OF DOPED PA FROM THE CHANGES IN PARAMAGNETIC SUSCEPTIBILITY AND FROM THE ESR SPECTRA

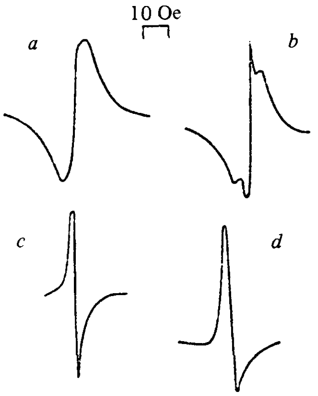

Figure 5. ESR spectra of *cis*-[CH(AsF$_5$)$_y$]$_x$ at room temperature and different dopant concentrations: (*a*) pure PA, (*b*) $y = 5 \times 10^{-4}$, (*c*) $8 \times 10^{-3} \leq y \leq 2 \times 10^{-2}$, (*d*) $y = 0.08$ (Ref.95).

The addition of the dopant Z (at concentration§ y) to PA produces a doped PA of composition (CHZ$_y$)$_x$ which has some of the properties of a metal, including electrical conductivity. According to Dyson's general theoretical considerations[90] on paramagnetic additives in metals an increase in y for (CHZ$_y$)$_x$ can result in asymmetry of the ESR line. In a large enough sample of doped PA, for which the sample thickness is greater than the depth of the skin effect at the ESR frequency, a typical Dyson (asymmetric) ESR line is observed (see Fig.5).[83,86,91–95] If the PA sample is thinner than the skin layer the line stays symmetrical even at high values of y.[96–99] Some workers[3,96,97] observed only one ESR line in PA doped with Li, Na, or Br$_2$, others[84,86,91,95,98] found two lines for p- and n-type dopants at low y, with different widths and a g-factor equal to that of the free electron, but at high doping levels ($y \geq 0.03$) only one line was observed (Fig.5). The combination of a broad and a narrow line is characteristic of different dependences of the intensity and shape of the line on the temperature, u.h.f.

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§ The concentration y is defined as the number of molecules of dopant per CH unit.

power, and on the presence of NH_3 impurities. The broad line has been assigned[86,91,95,98] to a *trans* fragment in *cis*-PA, and the narrow line to *trans*-PA. According to some workers[86,95,97,98] the change in shape of the ESR line of *cis*-PA as a function of y suggests a large non-uniformity in the distribution of the dopant in the polymer, uniform doping in *cis*-PA being effectively impossible because of the presence of segments of the *trans* isomer. In this sense *trans*-PA is more easy to dope uniformly, but even for this isomer we can only expect a moderate degree of uniformity in the distribution of dopants in the sample.

According to Shirakawa[42] the Curie paramagnetic susceptibility χ_C is very sensitive to the degree of doping non-uniformity: the more uniform the dopant distribution, the lower is χ_C. Various methods of doping have been suggested to improve the uniformity: slow doping at low pressure,[36,37] cylic doping,[95] modified doping,[3] electrochemical doping,[96] etc. The structure of the dopant and its physicochemical properties[95] can also affect the doping uniformity.¶ The I_3^- ion is a linear cylindrical molecule with a diameter of 3.37 Å, and behaves as a weak electron acceptor; AsF_5 and SbF_5 are octahedral [owing to fluorine sharing (Editor of Translation)], with a maximum diameter of 6.24 Å, and have high oxidising power. These properties of AsF_5 and SbF_5 hinder their penetration into the fibrils, and therefore doping with iodine is more uniform than doping with AsF_5 or SbF_5. The formation of a concentration gradient of dopant within the fibril has been suggested[37] as part of a simple model of the dopant distribution which gives a good agreement between calculated and experimental values of the magnetic susceptibility.

Studies[86,91,95] of the ESR spectral changes of *cis*-PA caused by doping showed that doping can initiate *cis–trans* isomerisation, and that this effect is a characteristic of PA. Electrochemical doping of *cis*-PA with lithium did not produce significant changes in the intensity of the ESR signal.[91,96] Doping (like isomerisation) takes place at the surface of the sample in the initial stages). This accounts for the appearance of a compensation effect† in the ESR signal in the initial stages, resulting in slight swelling of the polymer and a small change (by ~15%) in the *cis*/*trans* isomer ratio.[86,95] Lengthy exposure to the dopant results in diffusion along the fibrils,[86,91] which is a slow process, and the *cis-trans* isomerisation now takes place in the bulk of the sample. At this stage of doping the concentration of defects can no longer be significantly decreased by compensation effects.[86]

A threshold concentration of dopant is needed to initiate the isomerisation;[91,96] its value is largely determined by the chosen doping technique.

It has been reported[91] that high rates of introduction of the additive yield smaller y values than lower rates. This is because at high rates the concentration of dopant on the fibril surface can rapidly reach the value which initiates isomerisation. At low doping rates there is time for the dopant to diffuse into the fibril and reach a *trans* segment. Since in *trans*-PA the oxidation potential (ionisation potential) is slightly lower[96] than in *cis*-PA we may expect preferential doping of the *trans* segment. In PA samples containing a large proportion of the *cis* isomer the addition of impurities at first initiates *cis–trans* isomerisation, followed by doping of the *trans* segments. The slight inconsistencies between the threshold values (y) of the dopant concentration reported by different workers can be attributed to differences in the isomer composition of the initial sample or to differences in the doping techniques.[91]

The isomerisation process is followed by charge transfer to the paramagnetic defect, which converts it into the diamagnetic state. This mechanism was established[91] from the time-changes of the ESR spectrum after doping. If the doping process is stopped at the instant when two superimposed singlets appear, after some time (~1 h) the narrow singlet from *trans*-PA disappears, leaving only the signal from *cis*-PA.

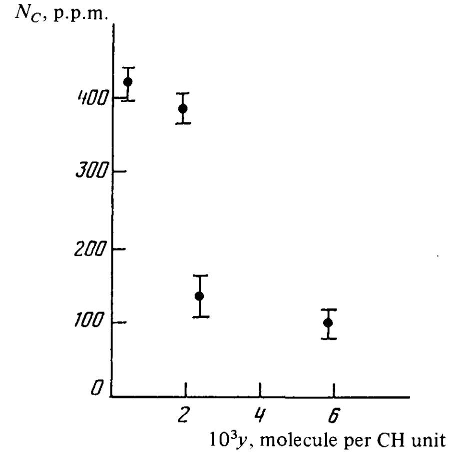

Figure 6. Change in the concentration of Curie spins N_C with the concentration of $AsF_5(y)$ in *trans*-PA (Ref.36).

By combining the ESR method with the Faraday compensation method it was shown that the addition of dopants to the *cis* and the *trans* isomers affects the nature and magnitude of the paramagnetism.[18,20,35-39,83,86] Thus, adding AsF_5 to *trans*-PA was found[36] to lower χ_C more than 400-fold for an increase in dopant concentration from 0.001 to 0.05. The change in spin concentration N_C corresponding to the paramegnetic Curie susceptibility for low concentrations of AsF_5 is shown in Fig.6. For *cis*-PA lightly doped with lithium ($y < 0.003$) the parameter χ_C decreases as y increases.[91] Under these conditions the temperature-independent Pauli paramagnetism is still insignificant (Pauli paramagnetic susceptibility $\chi_P \leq 5 \times 10^{-8}$ cm^3 mole^{-1}). In PA samples with a high concentration of AsF_5 only Pauli paramagnetism was observed[18-20,23,25,35-37,83,93] ($\chi_P \cong 10^{-6}$ cm^3 mole^{-1}). Doping with iodine did not produce Pauli paramagnetism even at high dopant concentrations.[38,39,99] Using AsF_5,[20,36] I_2,[37] and Na[97] as dopants produced a discontinuous increase in χ_P at concentrations in the region of 0.04–0.07. Fig.7 shows the dependence of χ_P on y[100] for samples doped with I_2 and AsF_5, and also the dependence of the conductivity σ on y. Clearly, we have a concentration range ($y < 0.05$) in which χ_P is still small but σ is already approaching the value corresponding to the metallic state. In contrast to

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¶ See also J.C.W.Chien, J.M.Warakomski, and F.E.Karasz, J.Chem.Phys., 1985, v.82, p.2118.

†The compensation effect can be described as follows: at low doping levels the effects of donor (or acceptor) additives are suppressed by the subsequent addition of impurities of the "opposite" type i.e. acceptor (or donor) additives respectively.

this report, Pauli paramagnetism was observed[35] at very low concentrations of AsF_5 ($y \cong 0.005$), coupled with a smooth increase in χ_P with increasing y. Later work[101] showed the reason for this discrepancy between the experimental results. In Ref.35 the concentration of paramagnetic centres was determined by the ESR method, which gives a large error in the double integration due to the large asymmetry of the line. In Refs.36 and 100 the Schumacher–Slichter method[102,103] was used, which allows the absolute value of the paramagnetism to be calculated more precisely than the ESR method.

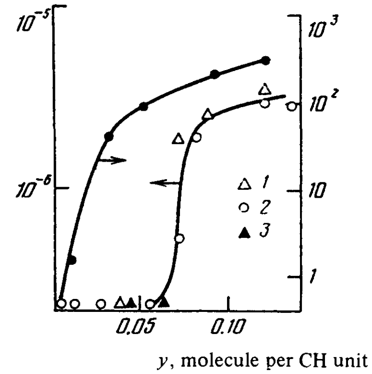

Figure 7. Dependence of the Pauli magnetic susceptibility χ_P and of the conductivity σ on the concentration of AsF_5 and I_3^- dopants.[100] The χ_P value for AsF_5 was obtained by the Faraday method (*1*) and from ESR data (*2*); the value for I_3^- by the Faraday method (*3*).

It has been suggested[4] that the carriers of charge and of paramagnetism are different species in PA, since the conductivity and the magnetic susceptibility have different temperature dependences: $\sigma \propto \exp(-AT^{-1})$ and $\chi_C \propto T^{-1}$. Other workers[19] came to the same conclusion. No correlation was observed[20] between the increase in magnetic spin susceptibility and the increase in σ when small amounts of AsF_5 were added to *trans*-PA (see also Fig.7). Different views are held at present on this behaviour of the electrical and magnetic characteristics of doped polyacetylene.

Some workers[19,20,36,37] interpret their experimental results on the changes in magnetic susceptibility of lightly doped PA in terms of the neutral soliton model.[56,89] However, a detailed examination of the experimental data from this standpoint reveals a number of inconsistencies (see, for example, Refs.20 and 54). Furthermore, neither the results of experiments with strongly doped PA nor the existence of a transition region in the $\chi_P(y)$ relationship are explicable in terms of the soliton model.

An alternative model[18,35] assumes the formation of metal-like regions, analogous to metal granules embedded in a dielectric. However, the application of this model also encounters serious difficulties.

IX. STRUCTURAL CHARACTERISTICS OF PURE AND OF DOPED PA FROM ^{13}C NMR DATA

The NMR signal from ^{13}C nuclei (at their natural enrichment level of 6%) for pure PA, obtained by rotation through the "magic angle", is a narrow line located at 127 p.p.m. for *cis*-PA and 137.4 p.p.m. for *trans*-PA (relative to the Me_4Si signal).[51,52,104] In samples of *trans*-PA with a 30% enrichment in ^{13}C a weak additional peak is observed at 47 p.p.m. (its intensity is 3.4% of that of the main peak). This peak has been attributed[104] to carbon atoms in a state of sp^3 hybridisation, i.e. the carbon atoms of the methylene groups. These groups interrupt the continuous conjugation of the polymer chain, giving an average length of the conjugated regions in *trans*-PA of about 30 CH groups. A content of methylene groups of 3.4% is confirmed by the element analysis, according to which the formula of PA is more accurately written as $(C_{1.00}H_{1.03})_x$ than as $(CH)_x$.

The changes in intensity, shape, and position of the two ^{13}C NMR peaks (127 and 137 p.p.m.) produced as a result of *cis–trans* isomerisation by heating pure *cis*-PA have been studied.[104] The *cis*-PA line is lowered by heating, but its width and position are unaffected. The *trans*-PA line undergoes changes in width and position (by ~1 p.p.m.) as the amount of *trans* isomer increases. This has been interpreted[104] as evidence that 1) the structure of partially isomerised *trans*-PA is different from that of pure *trans*-PA, and very inhomogeneous, and 2) the *cis* isomer has an ordered structure.

Nutation NMR[105] on pure PA prepared from acetylene enriched in ^{13}C (initially containing 6% of $H^{13}C{\equiv}{}^{13}CH$ molecules) showed that two types of bond are present in *trans*-PA, of length# 1.37 and 1.43 Å. The splitting in the nutation NMR spectrum of the two peaks corresponding to these bond lengths is ~300 Hz. If fast interconversion of the two types of bond were possible (as the soliton model stipulates) the two peaks would be replaced by a single peak. Hence we conclude that the interconversion does not take place, or that it takes place slowly (with a frequency much lower than 300 Hz).

Measurements of the second component of the ^1H NMR proton line led to the conclusion[106] that even a small concentration of I_2 ($y \cong 0.05$) causes almost complete *cis–trans* isomerisation, whereas according to ^{13}C NMR data the isomerisation is not complete even at higher doping levels.[107–111] This discrepancy may be attributed to differences in doping method (see Section VIII).

Studies of the ^{13}C NMR spectra of samples of composition *trans*-$[CH(AsF_5)_{0.076}]_x$ and *trans*-$[CHK_{0.09}]_x$ showed[108] that the line shifts produced by doping towards lower fields (+9 p.p.m.) for AsF_5 and towards higher fields (−12 p.p.m.) for K (relative to the line for pure *trans*-PA) are chemical shifts (as also stated in Ref.109). In some earlier work[100,110] a different interpretation of these shifts had been proposed: the Knight shift. However, the Knight shift calculated[108] for these concentrations is only +2 p.p.m. Thus doping produces a change in the π electron density on the carbon atoms. As the π electron density is decreased (or increased) by one electron in the calculation the shift of the ^{13}C NMR line towards lower (or higher) fields is ~160 p.p.m. The reported[108] chemical shifts are satisfactorily consistent with the theoretical estimates (+12 and −14 p.p.m.) for the concentrations of AsF_5 and K used in those experiments.

The analysis of the ^{13}C NMR spectrum of the *trans*-$(CHI_{0.08})_x$ sample[108] showed (allowing for the fact that the true dopant was the I_3^- ion) that practically all the iodine atoms are converted into the I_3^- state and contribute to the charge transfer, and also that the peak at 47 p.p.m. for sp^3 hybridised carbon atoms is significantly stronger than in pure PA. This suggests a very slight degree of chemical compound formation between the iodine and the polymer,

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#Similar values for the length of the C–C bonds were obtained by M.J.Duijvestijn, A.Manenchijn, J.Smidt, and R.A.Wind, J.Magnetic Resonance, 1985, v.64, p.461.

giving the fragment –CHI–. The volume of the undoped region was estimated[108] as 50%, since in the doped region the concentration of dopant was about double the average.

The ^{13}C NMR spectra for *trans*-$(CHBr_y)_x$ with $y = 0.661$ and $y = 0.103$ contain strong peaks in the 50 p.p.m. region. This indicates not only a high level of chemical compound formation between the bromine and the polymer (formation of the –CHBr– fragment) but also the formation of cross-links between neighbouring polyacetylene chains (the C atoms in the region of the cross-links are also in the sp^3 hybridisation state).[108]

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The results of magnetic resonance studies have given valuable information on the structure and properties of pure and of doped PA. The average length of the continuous conjugation regions in the polymer chains has been determined (about 30 CH units), and the alternation of bond length in the chain has been confirmed. It was shown that the paramagnetic centre or defect mainly responsible for all the magnetic properties of PA is the π electron. The delocalisation region of the paramagnetic π defect is found to vary between 7 and 93 CH units. In the *cis* isomer the paramagnetic defects are immobile, but in the *trans* isomer they are mobile at $T \geqslant 50$ K and immobile at $T \leqslant 50$ K. Doping produces various structural and chemical changes in PA (*cis–trans* isomerisation, chemical changes of the dopant additives, reaction of the additives with the polymer, etc.). None of the models so far proposed can explain all the results obtained by magnetic resonance methods for PA: there is no generally accepted account of the mechanism of electronic and nuclear relaxation, various estimates of the size of the delocalisation region of the unpaired π electron are inconsistent, and existing models of the paramagnetic defect cannot explain the extensive group of reported magnetic measurements in a manner consistent with the results of electrical measurements. The ^{13}C high-resolution NMR method (and some of its modifications) appear to be the most promising approach to the structural study of PA.

While this review was being prepared the proceedings of two international conferences and of an international school on organic conductors, including PA, were published.[112–114] Most of the recent publications are new developments of previously formulated ideas, and they do not affect the main conclusions of the present review on the structure of PA. However, two recent papers deserve special mention for suggesting new ideas as well as improved experimental approaches.[115,116]

Holczer and co-workers[115] suggested that many of the effects observed in *trans*-PA could be attributed to surface phenomena, determined by specific aspects of the morphology of the polymer. Calculation shows that in PA synthesised by Shirakawa's method, with a specific surface of 10–100 $m^2 g^{-1}$, ~20% of all the chains (1/5 of the total volume) are in contact with the surface, whereas in a normal solid the proportion of the atoms located in the first surface layer is $\sim 10^{-8}$.

Chien and Schen[116] studied by ESR the effect of the molecular weight (MW) of PA on the magnetic properties. They found that many of the characteristics of PA (concentration of paramagnetic centres in undoped and in doped PA, relaxation times T_{1e} and T_{2e} in the doped isomers) are insensitive to changes in MW between 500 and 870 000. However, in undoped PA the time T_{1e} decreases as the MW increases.

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The Radiation Polymerisation of Monomers Adsorbed on Solid Surfaces

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The present state of the study of the processes involved in the polymerisation, initiated by radiation, of monomers adsorbed on solid surfaces has been examined. Particular attention has been paid to the results of work on the quantitative description of the elementary stages of polymerisation on a surface.

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I. INTRODUCTION

The processes involved in the polymerisation of monomers adsorbed on solid surfaces have attracted considerable and increasing attention from research workers in the last 20 years. Interest in these reactions is due chiefly to their possible use for the solution of a number of practical problems. These processes are potentially convenient for modifying the surface properties of various solids (in particular mineral fillers, pigments, and chromatographic sorbents) and obtaining new materials (graft polymer fibres, films, and membranes, organic and mineral–organic ion-exchange materials, textile materials of various kinds, etc.).[1–4] In recent years there has been considerable interest in these reactions in connection with the problems of obtaining composite materials by polymerisation filling[5–7] and encapsulation.[8,9] The investigation of the characteristic features of the elementary stages of the polymerisation of monomers on a surface, and their relationship to the nature of the adsorption interaction of the monomers and polymers and the nature and actual structure of the solid support, is undoubtedly of independent scientific importance.

These reactions are initiated using special initiators,[10–14] ultraviolet radiation,[15,16] the mechanochemical method,[17] or an electric discharge.[18] Forms of ionising radiation, namely gamma-rays, X-rays, and fast electrons, are extremely convenient and are widely used in research practice. The processes of radiation-initiated polymerisation on a surface have now probably been most extensively studied. The examination of these processes is the main subject of the present review, which deals chiefly with the reactions involved in the radiation polymerisation of monomers on the surface of inorganic solids in adsorption systems of the "open" type. Polymerisation in clathrate complexes and inclusion compounds, which may be called adsorption systems of the "closed" type, was examined in Refs.19–22.

The topics examined in the present review have been dealt with to some extent in a number of review papers.[1,5,23,24] They have been examined most systematically (from data published up to 1972) in Ref.1; a fairly extensive bibliography is given in Ref.23. All these papers analyse chiefly the overall kinetic relationships for the processes involved in polymerisation on a surface. This is mainly due to the fact that studies of the mechanism and characteristics of the elementary stages in these reactions have been carried out only in recent years. In the present review, particular attention is paid to the results of studies of the elementary stages of the polymerisation. It may be noted that many of the conclusions about the characteristics of the elementary stages of radiation polymerisation on a surface, in particular the reactions of chain growth, transfer, and termination, also apply when other methods of initiation are used.

The reactions examined in the present review are described in the literature in different ways: polymerisation at a "gaseous monomer–solid" interface, grafting from the vapour phase or gas-phase graft polymerisation, polymerisation in adsorption layers, thin-layer polymerisation, etc. All these terms essentially refer to systems consisting of a solid, a monomer adsorbed on its surface (at different degrees of surface coverage, from fractions of a monolayer to tens and hundreds of monolayers), and the vapour of the monomer, present in equilibrium. The present review deals chiefly with systems in which a strong specific interaction between the polymerising group (the C=C bond) of the monomer and the solid (characteristic, in particular, of heterogeneous-catalytic polymerisation) does not take place. In most systems the main contribution to the adsorption interaction with the surface is made by the substituent at the double bond.

II. GENERAL REGULAR FEATURES OF POLYMERISATION ON A SURFACE

1. The Nature of the Active Centres of Polymerisation

The processes involved in radiation polymerisation on a surface have been studied chiefly in the temperature range from −50 °C to +100 °C. Under these conditions, both ionic and radical polymerisation chains may develop.

a) Ionic polymerisation

The irradiation of solids may lead to the production on their surface of various ionic active centres, whose lifetime is usually much greater than that of the ionic active centres in liquid monomers. This fact increases the probability of the development of ionic polymerisation chains on the surface. Unfortunately, there have been comparatively few studies of the processes involved in ionic radiation polymerisation on a surface.

It has been established[25-29] that in the polymerisation of styrene (ST) on various silicon dioxide specimens, the process takes place by cationic and radical mechanisms simultaneously. The polymerisation was carried out at temperatures close to room temperature, in comparatively thick adsorption layers (5–7 monolayers). The proportion of polymer formed by the cationic mechanism increases with increase in the quantity of aluminium impurity in the SiO_2. In specimens containing 10^{-2}–10^{-3}% aluminium, this proportion is 60–80%; at an aluminium concentration of ~1%, practically all the polymer is formed by the cationic mechanism, and, other conditions being equal, the rate of the process is several times that in the absence of impurity.[28] The mechanism of polymerisation in these systems was established by analysing the molecular mass distribution (MMD) of polystyrene (PST) formed under different conditions, including the use of inhibitors of different kinds. The molecular masses (MM) of the PST obtained by the radical mechanism are 10^5–10^6, and those for the cationic mechanism 10^3–10^4. In agreement with this, the gel-chromatograms of the PST show clearly defined bimodal character. The formation of low-molecular-weight PST is inhibited by ammonia, and that of high-molecular-weight PST is inhibited by benzoquinone.[26] The total activation energy of the cationic polymerisation of ST on silica gel is close to zero, and the kinetic order of the reaction with respect to the dose rate is ~0.7 (in the range 0.03–3 Gy s^{-1}).[27] Most of the cationic PST (~90%) is not grafted to the silicon dioxide surface. The radiation-chemical yield of the cationic polymerisation is ~10^4.

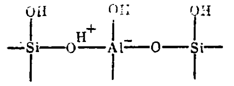
Similar results on the polymerisation of ST on SiO_2 were obtained in Refs.30–32. In an earlier paper,[33] however, a radical mechanism was proposed for the radiation polymerisation of ST on Degussa aerosil.

The low molecular masses of the cationic PST quoted in Refs.25–29 are attributed chiefly to non-degenerate chain transfer to the silicon dioxide surface, and in Refs.30–32 chiefly to effective chain transfer to the monomer. The two factors can apparently play a definitive role. It should be borne in mind, however, that the relative constant for chain transfer to the monomer in the cationic polymerisation of ST in the liquid phase is extremely high ($C_m \cong 2 \times 10^{-2}$ [34]); thus in polymerisation on a surface, chain transfer to the monomer alone may lower the MM of the cationic PST to the values observed experimentally.

In the analysis of the probability of the development of ionic chains in the polymerisation of a given monomer on a surface, it is necessary to take into account, in addition to other factors, the possible drying action of the solid on the system, due to the strong adsorption bonding of water.

The low-temperature radiation polymerisation of isobutene (IB) on silica gel (SG) has been studied.[35-37] The EPR spectrum of the IB–SG system, irradiated at −196 °C and −78 °C, indicates the presence of terminal polymer radicals $\sim\!-CH_2-\dot{C}(CH_3)_2$, showing that polymerisation takes place directly at the temperature of irradiation. The inhibiting influence of added methylamine on the yield of the terminal polymer radicals and the polymer indicates a cationic polymerisation mechanism. It is suggested that the terminal polymer radicals are formed as a result of the recombination of the growing cationic polymer chains with an electron liberated from a trap. The yield of these radicals depends on the IB concentration on the SG surface, and this dependence correlates with the concentration dependence of the yield of the polymer, determined gravimetrically after the temperature of the irradiated specimens had risen. In the region of the maxima on the two curves, corresponding to monolayer covering of the surface, the radiation-chemical yield of terminal polymer radicals at −196 °C is 1.5; the radiation-chemical yield of the inhibition of the polymerisation G_{in} was estimated by assuming that the number of these radicals is equal to the number of initiated polymerisation chains. It is important to note that the average number of polyisobutene macromolecules formed, determined from the values of the viscosity-average molecular masses ($M_\eta \cong 5000$), was found to be appreciably greater than the number of polymer radicals (by a factor of ~30), from which the authors correctly conclude that chain transfer reactions take place effectively during the polymerisation.

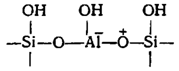
The following views were put forward[35-37] regarding the mechanism of chain initiation and transfer in the polymerisation of isobutene on silica gel. It is assumed that both processes are associated with the existence on the SG surface of Bronsted acidic centres, localised close to impurity aluminium atoms in tetrahedral configuration



$$-\mathrm{Si}(\mathrm{OH})-\overset{H^+}{O}-\mathrm{Al}^-(\mathrm{OH})-O-\mathrm{Si}(\mathrm{OH})-$$

(I)

The protons of these centres cannot initiate polymerisation in the absence of irradiation, since they compensate the negative charge of the aluminium atoms. On γ-irradiation, paramagnetic centres are formed in SG,[38] of the type



$$-\mathrm{Si}(\mathrm{OH})-O-\bar{\mathrm{Al}}(\mathrm{OH})-\overset{+}{\dot{O}}-\mathrm{Si}(\mathrm{OH})-$$

in which the hole is localised on an oxygen atom adjoining an aluminium atom. The proton of this centre is liberated, and can either capture an electron and be stabilised as a hydrogen atom, or add on to an IB molecule and form the carbonium ion $(CH_3)_3C^+$, which brings about polymerisation. The probable participation of the acidic surface centres of SG in the initiation of polymerisation is indicated by the fact that decrease in the acidity of the SG by preliminary treatment with alkali leads to a marked decrease in the yield of polyisobutene.[36]

It is suggested that the main contribution to the mechanism of chain transfer is made by the reaction of the growing macro-cations with the acidic centres of the SG surface of type (I), as a result of which the macro-cation neutralises the charge on the aluminium, and the liberated proton, by reacting with a monomer molecule, starts a new polymer chain. In the opinion of the authors,[35-37] the polyisobutene macromolecules are also formed as a result of the mutual recombination of terminal polymer radicals.

The results of studies of the radiation polymerisation of liquid monomers in the presence of various solid oxides,[39-44] examined in detail in Ref.39, are relevant to the subject of the present review. These studies were generally carried out under conditions in which the liquid monomer was poured over a layer of solid oxide powder; the concentration of the monomer was 40–80 mass %. In these studies, chiefly in work carried out in the Karpov Physicochemical Scientific

Research Institute,[39–41] the idea of a correlation between the semiconducting character of the oxides and the mechanism of polymerisation was put forward. It was shown that the *n*-type (electronic) semiconductors ZnO, TiO_2, and Cr_2O_3 facilitate the development of cationic chains, and the *p*-type (hole) semiconductors MgO, Cu_2O, and NiO the develpment of anionic polymerisation chains.

b) Radical polymerisation

Most studies carried out up to the present have dealt with monomer–support systems in which radiation polymerisation on the surface develops chiefly by a radical mechanism.[1,9,45,46] A radical mechanism of polymerisation is proved using data on the influence on the process of typical radical inhibitors (diphenylpicrylhydrazyl, O_2, benzoquinone) [33,45]† and data on the compositions of the copolymers and the kinetics of copolymerisation on a surface,[47,49] and on the micro-structure of the polymer chains formed.[47] Thus the processes involved in radical polymerisation on a surface have been studied in most detail. Subsequently, unless otherwise stated, radiation polymerisation by a radical mechanism is discussed.

2. The Adsorption Mechanism of Polymerisation

One of the first questions arising in the analysis of the mechanism of polymerisation on a surface, as in the analysis of other surface reactions, is the question of whether this reaction takes place by an "adsorption" mechanism or by a "collision" mechanism. In the first mechanism, the monomer molecules are adsorbed, migrate over the surface, and finally are added on to the active centre situated on the surface (the active terminal unit of the growing chain); the "working" concentration of the monomer is its concentration in the adsorption layer. In the second mechanism, the acts of chain growth take place when monomer molecules from the vapour phase collide directly with the active centre; here, the "working" concentration is the monomer concentration in the vapour phase.

The mechanism of polymerisation was a subject of discussion in the mid-sixties. In Refs.33, 45, and 46 it was concluded from overall kinetic data that polymerisation on a surface takes place by an adsorption mechanism. The main evidence was the decrease in the rate of polymerisation with increase in temperature at a constant monomer vapour pressure. The collision mechanism of polymerisation was developed in Refs.16, 50, and 51. In the opinion of these authors, this temperature dependence of the rate of polymerisation may be due to the destruction of active centres with increase in temperature, and a corresponding decrease in the rate of initiation of polymerisation.[50]

The results in Refs. 9, 47, and 53–55 apparently prove that polymerisation takes place by an adsorption mechanism in the systems studied. The dependence of the rate constants of chain growth k_g on the mechanism of adsorption and on the nature of the adsorption bonding between the monomer and the support, observed in these studies, can be understood only by assuming an adsorption mechanism of polymerisation. For example, as established in Refs.47 and 54, the change in the heat of adsorption of vinyl acetate (VA) on AS/400# in the range of coverage of about half a monolayer is accompanied by a fairly sharp (several-fold) change in k_g. An important feature is that this change in k_g at different temperatures (20 °C and 50 °C) takes place in approximately the same range of coverage, whereas the pressures in the vapour phase, corresponding to this range of coverage, differ by a factor of more than 20.

If the calculations are carried out using as working concentration the surface concentration of adsorbed monomer σ, the temperature dependence of the value of k_g for radical polymerisation is described by the Arrhenius equation with "normal" values of the activation energy of growth E_g.§ Similar calculations using the concentration of the monomer in the vapour phase give negative or anomalously low values of E_g.

In later papers on polymerisation on a surface from the vapour phase,[16,50,51] the authors conclude that polymerisation takes place by an adsorption mechanism.[52]

3. Thermal and Diffusion Processes Accompanying Polymerisation on a Support

For a correct analysis of the kinetics of polymerisation on a surface, it is necessary to estimate correctly the role of macrokinetic factors, such as, in particular, the possible non-isothermal nature of the process and the diffusion retardation in the transport of the monomers in real adsorbent specimens (porous granules, tablets, layers of powder, etc.). Unfortunately, in many papers these factors are not properly analysed.

When the dose rate is not too high, the heating of the specimens in the radiation field, not associated with polymerisation, is usually insignificant. At dose rates of 1–10 Gy s^{-1}, it generally does not exceed fractions of a degree. In the analysis of the possible non-isothermal nature of the system resulting from the heat liberated on polymerisation, it must be borne in mind that although the reaction zone usually makes up only a small fraction of the total volume of the specimen, a significant increase in temperature is possible, because of the low thermal conductivity of the specimens. For specimens of silicon dioxide in the form of tablets or powder with a specific surface of ~200 m^2 g^{-1}, a layer porosity of 80–90%, and characteristic layer dimensions of 0.5–1 cm, the increase in temperature as a result of the polymerisation of MMA and VA for monolayer coverage of the surface and dose rates of the order of 1 Gy s^{-1} is 1–10 K.[56] The increase in temperature increases considerably with increase in the degree of coverage of the surface by the monomer.

The correction to the stationary rate of polymerisation ν_{st}, taking account of the increase in temperature, in the case of experiments in a closed system with a small vapour phase volume ("without maintenance") can be calculated from the expression[57]

$$\nu_{st}/\nu_{st,0}=\exp\left[-\frac{E}{R}\left(\frac{1}{T_0+\Delta T_\infty}-\frac{1}{T_0}\right)\right]\simeq 1+\frac{E}{RT_0^2}\Delta T_\infty$$

---

†Because of the decrease in the "activity" of most inhibitors on a surface,[48] the quantities of inhibitor which are effective are much greater than the stoichiometric quantities.

#Here and subsequently, AS/200, AS/400, etc. denote aerosils treated in a vacuum at 200 °C, 400 °C, etc.

§Thus for example the values of E_g for the polymerisation of VA and methyl methacrylate (MMA) on an aerosil at a monolayer coverage of the surface by monomers are 17 kJ $mole^{-1}$ and 32 kJ $mole^{-1}$ respectively.[55]

where T_0 is the temperature of the thermostat, ΔT_∞ the stationary increase in temperature, E the total activation energy of the process, and $v_{st,0}$ the stationary rate under isothermal conditions. The quantity ΔT_∞ is related to the effective heat of polymerisation $-\Delta H_{eff}$ by the expression

$$\Delta T_\infty = \frac{-\Delta H_{eff}}{c}\,\frac{v_{st}}{a}$$

where c is the heat capacity of the system, and a an experimentally determined parameter characterising the rate of removal of heat from the specimen.

It is more difficult to take account of possible non-isothermal character in experiments in an open system "with maintenance", when an increase in the temperature of the specimen leads to a decrease in the equilibrium concentration of the monomer on the adsorbent; it is then necessary to solve simultaneously the equations for the kinetics of polymerisation, adsorption, diffusion, and thermal conductivity.

The influence of diffusion retardation in the layer of adsorbent on the stationary kinetics of polymerisation can be examined further. When the polymerisation is carried out under conditions in which the formation of the polymer produces a diffusion flux of the monomer in the specimen, the influence of diffusion retardation on the observed stationary rate of polymerisation (v_{st}) is revealed by a deviation of the distribution of the monomer concentration $\sigma(x)$ along the cross-section of the specimen from the equilibrium distribution, leading to a decrease in the observed rate of polymerisation, which starts to depend on the specimen thickness L. In those cases where the average decrease in the monomer concentration $\overline{\Delta\sigma}$ in the specimen is small compared with the equilibrium adsorption σ^*, the rate of polymerisation can be taken as approximately constant over the cross-section of the specimen. $\sigma(x)$ is then described by a simple parabolic law, and $\overline{\Delta\sigma}$ is given[56] by the expression:

$$\overline{\Delta\sigma} = v_{st}L^2/12D_{eff}$$

where D_{eff} is the effective diffusion coefficient of the monomer in the specimen. The coordinate x is measured from the centre of the specimen. The magnitude of the deviation has been analysed,[56] and it was shown, in particular, that in the polymerisation of VA, MMA, and ST on aerosil tablets with a thickness of ~2 mm, compressed at a pressure of 300 kg cm^{-2}, for degrees of coverage by the monomer of about one monolayer, a temperature of 50 °C, and a radiation dose rate of 0.35 Gy s^{-1}, the value of $\overline{\Delta\sigma}$ does not exceed 10% of σ^*.

In the case of polymerisation at low concentrations of adsorbed monomer, however, when it is necessary to carry out the reaction to degrees of conversion close to or greater than σ^*, the influence of diffusion retardation on the observed rate of polymerisation may be considerable. Decrease in the monomer concentration leads to a marked decrease in the value of D_{eff}, and this in turn also increases the influence of diffusion on the rate of polymerisation at low concentrations. Under these conditions, the dependence of the rate on the coordinate x cannot be neglected, and the distribution of the monomer concentration over the cross-section of the specimen for linear termination of the kinetic chains is described by the expression:[58]

$$\sigma(x) = \sigma^* \frac{\mathrm{ch}\{[(k_g/k_x)(v_i/D_{eff})]^{1/2}x\}}{\mathrm{ch}\{[(k_g/k_x)(v_i/D_{eff})]^{1/2}(L/2)\}}$$

where v_i is the rate of initiation, k_g the chain growth rate constant, and k_x the rate constant for linear termination. The observed rate of polymerisation is proportional to $1/L$.

4. Overall Kinetics of Polymerisation

The influence of the support on the rate of polymerisation of monomers on a surface can be examined first. Table 1 gives the values of the radiation-chemical yields for polymerisation in various systems, calculated from published data.[32,47,56] A noteworthy feature is the high values of the polymerisation yields calculated per unit of energy absorbed by the adsorbed monomer, G^*_{pol}; they are much greater than the values for the polymerisation of the same monomers in the bulk.¶ Similar results were obtained in other studies (see Ref.1). Thus for a number of systems, the supports have an appreciable accelerating action on polymerisation. The mechanism of this action will be examined below.

Table 1. Some overall kinetic characteristics of the radiation polymerisation of monomers on a surface (coverage of the surface by monomers about one monolayer, temperature 50 °C, dose rate 0.35 Gy s^{-1}).[32,47,56]

Monomer	Adsorbent	n_i^*	$10^{-4}\,G_{pol}$	$10^{-4}\,G^*_{pol}$	$10^{-4}\,G^b_{pol}$
VA	AS/400	1	0.7	12	3.5**
VA	AS/700	1	0.6	10	3.5**
VA	AS/900	0.8	—	—	3.5**
VA	MAS***	0.5	2.0	120	3.5**
MMA	AS/400	1	0.6	10	0.9
MMA	AS/200	1	1.0	15	0.9
MA	AS/400	1	2.6	43	7**
BMA***	AS/400	0.8	0.3	5	0.6
ST	AS/400	0.7	0.3	10	0.04**

Notes. The specific surface of the adsorbents is ~200 m^2 g^{-1}. The polymerisation of all the monomers except ST takes place by a radical mechanism; the polymerisation of ST takes place by cationic and radical mechanisms simultaneously on an aerosil surface, and by a radical mechanism in the bulk. Notation: G_{pol} and G^*_{pol} are the radiation-chemical yields of polymerisation on a surface, calculated per 100 eV of energy adsorbed by the entire system and by the monomer respectively; G^b_{pol} the radiation-chemical yield of polymerisation in the bulk ("in the mass") in the initial stages; MA = methyl acrylate; BMA = butyl methacrylate.

*Dose rate range studied 0.05–5 Gy s^{-1}.

**Calculated from published data.[95]

***Methylated aerosil; specific surface ~60 m^2 g^{-1}.

****Temperature 25 °C.

Analysis of the available data shows (see for example Table 1) that in polymerisation on a surface, in contrast to processes in the liquid phase, linear termination of the kinetic chains is observed extremely frequently (the order for the dependence of the reaction rate on the irradiation dose rate, $n_i = 1$); the reasons for this will be examined below.

¶ The values of G^*_{pol} are proportional to the relative or reduced rate of polymerisation v/σ, expressed as fractions of the original quantity of the monomer on the surface in unit time (for example in s^{-1}).

The specific mechanisms of linear termination may be different in different systems. For the polymerisation on an aerosil of vinyl acetate and various other monomers with highly active growing radicals, the mechanism apparently involves degenerate chain transfer to the hydroxide groups of the surface and the formation of radicals whose activity is much lower than that of the growing macro-radicals; kinetically, this appears as chain termination.[47,59] This mechanism is confirmed, in particular, by the fact that with decrease in the concentration of hydroxide groups on the aerosil surface, for example as a result of an increase in the temperature of treatment to 900 °C, the rate of termination in the polymerisation of VA decreases, and n_i deviates from 1 towards lower values.[56] On a methylated aerosil not containing hydroxide groups, $n_i = 0.5$, that is quadratic termination of the kinetic chains takes place.[47] A similar mechanism of termination has been assumed[33] for the polymerisation of MMA on an aerosil; with increase in the quantity of polymer formed on the surface, n_i decreased from 1 to 0.5.

Chain termination associated with the occlusion of the growing macro-radicals is apparently fairly common. Complete "burial" of the growing active centre is not essential. A sufficiently marked decrease in the specific growth rate, due to a decrease in the local concentration of the monomer close to the active centre, will appear kinetically as chain termination. As an experimental indication of the role of occlusion phenomena in chain termination, data[60] on the radiation polymerisation of acrylonitrile (AN) on alumina fibres can be considered. n_i changes from 0.5 to 1 on going from the non-porous to the fine-porous fibre. An occlusion mechanism has been proposed for the deactivation of the growing macro-radicals in the polymerisation of acrylic acid on kaolin.[61] An occlusion mechanism of chain termination in the polymerisation of AN on KSK-2 silica gel was established by EPR.[62] Post-polymerisation and EPR methods have shown that in the polymerisation of MMA on an aerosil at a temperature of 25 °C, kinetic termination of all the growing radical chains is not accompanied by chemical destruction of the macro-radicals; for reasons which are not yet completely clear, the growing macro-radicals at a definite moment undergo occlusion immobilisation, as a result of which the specific growth rate decreases by a factor of ~300; with increase in the temperature of the system (for example to 70 °C), "reanimation" of the kinetic chains is observed.†

There are probably several forms of occlusion, for example: 1) self-occlusion of the chains in the fine pores as a result of the covering of the transport "windows" of the pores as chain growth proceeds; 2) occlusion in pores with small windows (particularly in dead-end pores), taking place as a result of the growth of other chains, which prevent the transport of the monomer into the pore; in this case, as noted by Kabanov (see Ref.1), n_i may be less than 1. It is more difficult to picture the occlusion immobilisation of a macro-radical growing on an open surface. In some systems with extremely weak adsorption interaction of the units of the macromolecule with the surface, deactivation of the macro-radical may take place as a result of a conformational change ("collapse") from an unfolded chain to a compact globule with localisation of the active centre inside the globule. The actual mechanism of the occlusion termination of the growing chains in polymerisation on the surface of solids has not been established for any system.

Linear termination of the growing radical chains on impurities, for example iron ions, is also possible. As far as the mechanism of the quadratic termination of polymerisation chains on a surface is concerned, it is possible that, because of the obvious retardation of the thermal diffusion of the macro-radicals on the surface (see also section V), in some systems a "reactive" or "chemical" mechanism of diffusion will predominate, where the meeting of the growing active centres and their disappearance take place as a result of their movement over the surface during the actual growth reaction.

Study of the temperature dependence of the rate of polymerisation has shown that the corresponding activation energy E_{tot} in different systems varies from 0 to 40 kJ mole^{-1}, and usually decreases with increase in the degree of covering of the surface by the monomer.[55,63] The latter is related[55] to the corresponding decrease in the activation energy of polymerisation chain growth E_g (see section V and Table 3).

High kinetic orders of the polymerisation with respect to the concentration of the adsorbed monomer have been noted.[1,64] The authors cited relate these results to the formation of associates of the monomers on the surface of the support. These results, however, are fully covered by the general concept based on the dependence of the chain propagation rate constant on the nature of the adsorption bonding and also on the degree of covering of the surface by the monomer and the thickness of the adsorption layer; this concept is developed below (see sections V and VI).

III. MOLECULAR AND STRUCTURAL CHARACTERISTICS OF THE POLYMERS FORMED

1. Structural and Conformational Characteristics of the Macromolecules and Their Distribution on the Surface

The structure of the macromolecules formed and their distribution on the support in relation to the processes of radiation polymerisation on a surface has been the subject of special study only in recent years. The molecular mass distribution of the polymers formed in the polymerisation of ST and MMA on silica gels has been studied[25-29,65,66] by gel-permeation chromatography (GPC). The polymerisation was carried out at extremely high monomer concentrations and degrees of conversion. The results were used chiefly for the separate determination of the yields of radical and ionic, grafted and non-grafted polymers. The fraction of grafted PST is very low (15–20%), whereas for polymethyl methacrylate (PMMA) this fraction is 70–80%. Under the conditions studied, ST was polymerised chiefly by a cationic mechanism, and MMA by a radical mechanism. The proportion of grafted PST is higher if the polymerisation is carried out as a result of the post-effect after preliminary irradiation of the silica gel in a vacuum.[29] The influence of the monomer concentration on the MMD of polystyrene obtained by the radiation polymerisation of ST on silica gel has been examined.[31] GPC has been used[67] to study the molecular characteristics of PST formed by the radiation polymerisation of ST in the porous structure of wood.

In the initial stage of the polymerisation of vinyl acetate on aerosil (at degrees of conversion up to one third of an effective monolayer), linear macromolecules are formed, and $\bar{M}_w/\bar{M}_n \cong 2$.[68] On further polymerisation, effective branching of the macromolecules and marked broadening of the MMD take place. In the range of degrees of conversion from one third

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†See E.Ya.Yunitskaya, Candidate's Thesis, Karpov Physicochemical Scientific Research Institute, Moscow, 1986.

to two thirds of a monolayer (irradiation dose 0.3–0.6 kGy), the width of the MMD increases by a factor of ~3, and the degree of branching by a factor of 2.5. It is suggested that these changes are related to radiolysis of the polymer and chain transfer to the polymer.

Infrared spectroscopy has been used to study the conformational characteristics of the polymers formed in the polymerisation of VA and MMA on aerosil (AS/400 and AS/200), before their separation from the surface.[47,56] It was shown that a fairly high proportion of the units of the PVA and PMMA formed are joined to the aerosil surface by hydrogen bonds (between the CO groups of the polymers and the OH groups of the surface). The proportion of units bonded to the surface increases, in particular, with decrease in the monomer concentration σ at which the synthesis is carried out, and is 70–80% at a concentration lower than one quarter of a monolayer. This indicates that the macromolecules formed under the given conditions have unfolded conformations. If the polymerisation is carried out at high concentrations of the adsorbed monomer (several monolayers or more), the PMMA molecules on the surface apparently have the form of a non-planar coil.

The micro-structure of the macromolecules formed by polymerisation on a surface has been studied by high-resolution ^{1}H and ^{13}C NMR spectroscopy.[47,56] It was established, in particular, that PVA and PMMA synthesised on an aerosil have an atactic structure, similar to that of the polymers obtained by radical polymerisation in the liquid phase. At the same time, the PMMA obtained at low degrees of covering of the surface by the monomer (approximately one quarter of a monolayer) contains a higher proportion of isotactic triads.[56] This is apparently due to the stronger adsorption bonding of both the monomer and the polymer to the surface, and to the more rigid stereochemical control of the acts of chain growth at low values of σ. Poly-n-butyl methacrylate synthesised on an aerosil also contains a higher proportion of the isotactic structure than the liquid-phase radical polymer.[9]

The nature of the distribution of the resulting polymer on the surface is of considerable interest, particularly from the practical viewpoint. A number of authors report that this distribution is markedly non-uniform. In a study of the polymerisation of MMA and ST on MgO and an aerosil, it was concluded from kinetic data that more or less complete "overgrowth" of the surface of the support by the polymers takes place on the formation of 3–6 effective monolayers of the polymers on the aerosil, and 10–20 on MgO.[1,33]

The nature of the distribution of the macromolecules of PST, PMMA, and polyacrylonitrile (PAN) grafted to an MgO surface as a result of radiation polymerisation of the monomers from the vapour phase has been studied.[69,70] The size distribution of the MgO particles was studied by sedimentation in a hydrocarbon medium; the adsorption on the magnesium oxide powders of stearic acid, which can undergo irreversible adsorption on the non-modified regions of the MgO surface, and other characteristics, were also studied. The measurements showed that with increase in the quantity of grafted PST (from 1 to 25 effective monolayers), the aggregates of MgO particles in toluene gradually break down, since the surface of individual MgO particles becomes organophilic. The characteristic size of the aggregates changes from 20 μm to 0.5 μm; the size of an individual MgO particle is 0.01–0.1 μm, that is breakdown of the aggregates is still not complete. Even for the maximum quantity of grafted PST, approximately one third of the MgO surface is not covered by the polymer and retains its ability to absorb stearic acid. A similar picture is observed in the grafting of PMMA and PAN.

It was concluded[69,70] that the radiation grafting of the macromolecules on the surface of mineral carriers is "mosaic" in character. This was attributed to non-uniformity of the original surface; it was assumed that on the surface there are regions on which adsorption and hence polymerisation of the monomers does not take place. In Ref.1, the non-uniformity of the distribution of a grafted copolymer is related to the higher rate of initiation of grafting to the polymer already formed on the surface, compared with the original support. Further studies are required to obtain a more definite answer to the question of the reasons for the non-uniform distribution of polymers on a surface. In all cases, however, in the analysis of this question it is necessary, in particular, to take account of the actual conformation of the macromolecules on the surface.

2. The Efficiency of the Grafting of Macromolecules to a Surface

Even in the earliest papers on the "approach" radiation grafting of polymers from the vapour phase (see Ref.1), attention was drawn to the fact that this method, unlike grafting from the liquid phase, usually gives a very small quantity of homopolymer, indicating that the grafting of the macromolecules has a high efficiency. According to these data, the quantity of non-grafted polymer usually did not exceed 5% of the total concentration of polymer. These results were related to the fact that under the experimental conditions used in these studies (at a fairly low concentration of monomer on the surface), most of the active centres initiating polymerisation are produced from the material of the support, and this may lead to the production of a covalent bond between the macromolecules formed and the support at the initiation stage. It has also been suggested[1,45] that the low-molecular-weight radicals formed in the system on irradiation are unable to initiate polymerisation before their transfer to the vapour phase and disappearance, since the time for which they are present in the adsorbed state τ_a is small compared with the characteristic time of the act of polymerisation chain growth τ_g

$$\tau_a \ll \tau_g \tag{1}$$

It was subsequently established,[26,65,71] however, that the quantity of non-grafted polymer is usually much greater than indicated in the early studies, although it is sufficiently less than that for grafting from the liquid phase. In the polymerisation of VA, AN, and MMA on an aerosil it amounts to 10–50% of the total quantity.[71] In the analysis of these results it must be borne in mind that in most experiments, relationship (1) apparently is not fulfilled. Because of the porosity of real adsorbent specimens (layer of powder, porous tablet, etc.), the total time for which the low-molecular-weight radical is present in the adsorbed state during its diffusion over the specimen to the point of possible disappearance (τ_a^{Σ}), because of repeated re-adsorption on the pore walls, is usually greater than τ_g. Thus most of the low-molecular-weight radicals are able to take part in the polymerisation on the surface.[71]

The total time for which the diffusion species is present in a real specimen can be described by the relationship:[72]

$$\tau_D = l^2/3D_{\mathrm{eff}}$$

where l is half the thickness of the specimen. In typical systems with weak bonding, D_{eff} for the monomer molecules is 10^{-3}–10^{-5} cm^2 s^{-1}.[73] For low-molecular-weight radicals such as the radicals of chain transfer to the monomer and similar radicals, D_{eff} is usually of the same order of magnitude. In most experiments on polymerisation, the fraction of the surface diffusion flux of the monomer in the specimen is fairly high relative to the total,[73] so that τ_a^{Σ} is close to τ_D. Estimation of τ_a^{Σ} for the low-molecular-weight radicals which chain transfer to the monomer in the polymerisation of vinyl acetate on an aerosil (specimen in the form of a tablet with thickness 2 mm and porosity ~80%) gives the value ~10 s (for $\tau_a \cong 10^{-4}$ s), whereas $\tau_g \cong 10^{-2}$ to 10^{-1} s.[55,73] Naturally, the situation must be evaluated separately in each specific case with allowance for the above considerations.

In the analysis of experimental results from the viewpoint of the efficiency of grafting, account must be taken of a number of additional features. Thus the efficiency of grafting is determined by treating the specimens, after polymerisation, with solvents to extract the non-grafted polymer from the surface. To obtain correct results it is necessary to make the correct choice of solvent. On the one hand, it is necessary to take account of the fact that the compound used should not only be a good solvent for the polymer but also displaces it effectively from the adsorbent surface.[71] On the other hand, it is necessary to bear in mind the possibility of the hydrolysis, under the influence of the solvent, of the covalent bond between the macromolecule and the support, or hydrolytic rupture of the main chain of the macromolecule.[65,71,74] The hydrolytic instability of the $\geqslant\mathrm{Si{-}O{-}C}$ bond and the stability of the $\geqslant\mathrm{Si{-}C}$ bond have been noted.[74]

3. Secondary Reactions in the Polymer Chains Formed. The Radiolysis of Polymers on a Surface

An important characteristic feature of the processes involved in radiation polymerisation is that the macromolecules are subjected to the action of radiation for some time after their formation. Attention has been drawn[65,67,68] to the fact that in polymerisation on a surface, various manifestations of the radiolysis of the polymers are observed for very small radiation doses (less than 1 kGy). In polymerisation in the bulk, secondary radiation reactions in the polymers are usually not observed at such low doses. It has been established[68] that there is effective branching of PVA macromolecules on an aerosil, and marked broadening of the MMD in the dose range ~0.5 kGy. A decrease in the number-average values of the molecular mass was observed for PVA with increase in the polymerisation time at doses of ~1 kGy; it was suggested that this effect is due to the sensitising influence of the support on the radiolysis of the macromolecules. Attention has been drawn[65] to the radiation degradation of PMMA on silica gel at doses of 1.2–5 kGy; it was also concluded that this process is accelerated by the support, although the experimental data obtained by comparing the results of the irradiation of PMMA on a silica gel surface and in a "block", on the basis of which this conclusion was reached, are not completely correct, because of the marked differences in the molecular masses of the PMMA specimens compared. The accelerating action of the support on the radiation degradation of PST in the grafting of ST on wood has been reported.[67]

The special study of the radiolysis of polymers on solid surfaces, including the study of model systems in the absence of monomer, is of considerable interest. The action of radiation on PST deposited and grafted on silica gel has been studied.[75] It was shown, in particular, that radiation degradation of the grafted polymer takes place; the radiation-chemical yield of the ruptures is 2. The presence of the homopolymer suppresses the degradation. When PST is irradiated in a "block", cross-linking of the polymer takes place; $G_{c\text{-}l} \cong 0.17$.

Various characteristic features of the radiolysis of polymers deposited on an aerosil and undergoing degradation (PMMA) or mainly cross-linking (polymethyl acrylate, PMA), have been studied.[32]# The polymers were deposited on the aerosil by polymerising the monomers on the surface. The radiation-chemical yield of the ruptures of the main chains of PMMA, G_r^*, determined by measuring the molecular mass of the polymers viscosimetrically and recalculating to unit energy absorbed by the polymer, was much greater for irradiation on the aerosil, compared with the yield of ruptures for the irradiation of PMMA in a "block". When the quantity of polymer deposited on the aerosil is close to an effective monolayer, the value of G_r^* is 5–10 (depending on the conditions of synthesis and hence on the conformation of the macromolecules), whereas for the irradiation of PMMA in a "block", this yield is close to 1. G_r^* decreases regularly with increase in the quantity of polymer on the surface.

The radiation-chemical yield of polymer radicals G_R^* is also much higher for the irradiation of PMMA on a surface. At concentrations of PMMA on the aerosil of ~0.05 and ~0.5 effective monolayer, the initial yield of terminal radicals G_R^*, determined by EPR, has the values ~350 and ~70 respectively, whereas for irradiation of the specimen in a "block", this yield is 3–4. This is due chiefly to the effective transfer of the energy of the radiation, absorbed by the silicon dioxide particles, to their surface and to the polymer adsorbed on it. Similar effects were previously noted in a study of the radiolysis of adsorbed low-molecular-weight hydrocarbons.[76–79]

Another noteworthy feature is that under comparable conditions, G_R^* is much greater than $2G_r^*$. An appreciable proportion of the ruptures of the main chains is apparently localised close to the ends of the macromolecules, and are not detected by measuring the average molecular mass viscosimetrically.

The radiolysis of PMA on an aerosil surface has been studied for specimens containing ~2 and ~4 effective monolayers of the polymer.[32] The original molecular mass of the polymers ($\bar{M}_\eta$) was ~10^7. Irradiation of the specimen in a block leads to effective cross-linking of the PMA; for a dose of 1–1.5 kGy, the concentration of the gel fraction was ~50%. On irradiation on a surface with doses up to 10 kGy, gel formation is not observed, but effective degradation of the macromolecules takes place, and the initial yield is $G_r^* \cong 5{-}10$. On subsequent irradiation, a gel fraction gradually appears. The dose required for the formation of 50% gel fraction in the polymer on the support is 20–50 times that for the "block". It is suggested that this marked suppression of gel formation when PMA is irradiated on a surface is due to a change in the ratio of the yields of ruptures and cross-linkages in favour of the first process, and also to the characteristic topological features of the specimen (the small thickness of the polymer layer, and its distribution in "islets").

Thus the results indicate that there is a marked increase in the rate of radiation degradation and a change in the direction of the processes involved in the radiolysis of the polymers on the surface of silicon dioxide particles. These

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#See also M.A.Bruk, G.G.Isaeva, E.Ya.Yunitskaya, S.A.Pavlov, and A.D.Abkin, Radiat.Phys.Chem., 1986, 27, 79.

results are extremely important, not only for the investigation of the details of polymerisation on a surface but also for the study of the radiation stability of filled polymer materials and their modification by radiation.

IV. THE ADSORPTION AND MOLECULAR TRANSPORT OF MONOMERS ON A SURFACE. SYSTEMS WITH STRONG AND WEAK ADSORPTION BONDING

As noted in section II, radiation polymerisation on a surface usually takes place by an adsorption mechanism. The relation of the characteristic features of the elementary stages of the polymerisation, in particular the reactions of chain growth, to the nature of the adsorption and the surface mobility of the monomers and polymers is therefore a central question in the area being discussed. The analysis of adsorption equilibria and the molecular transport of the monomers in the specimens is also necessary to determine the true concentration of the monomers in the reaction zone.

The equilibrium adsorption of MMA and ST on an aerosil and on magnesium oxide has been studied on a McBain balance.[1] The published conclusion that the adsorption is monomolecular in these systems does not appear fully justified. The heats of adsorption of various monomers on KSK-2 silica gel have been determined calorimetrically.[80,81] The heats of adsorption decrease considerably with increase in the degree of covering of the surface (at degrees of covering less than a monolayer). The equilibrium adsorption of acrylic and methacrylic acids on kaolin has been studied.[61]

The adsorption equilibria, mechanism, and dynamics of the adsorption of a wide range of monomers on silicon dioxide specimens (chiefly aerosil and its modified forms) have been studied in detail.[47,56,73,82] On the basis of the results obtained, the authors cited divide the systems studied into two main groups. In the systems of the first group, the values of the heats of adsorption $-\Delta H_a$ are 30–90 kJ mole^{-1}, and the adsorption is non-localised, reversible, and characterised by a high surface mobility of the monomers. This type of adsorption on SiO_2 is shown by most of the vinyl monomers studied (VA, AN, ST, MMA, tetrafluoroethylene, etc.). These systems were called systems "with weak bonding".

The main adsorption centres on the silicon dioxide surface in these systems are surface hydroxide groups, which form hydrogen bonds with the polar functional groups of the monomer molecules (MMA, AN, VA, etc.) or weak π-complexes with a system of conjugated double bonds (ST). The strength of these adsorption bonds can be characterised to some extent by the magnitude of the displacement of the absorption band of the hydroxide groups of the surface in the region of 3750 cm^{-1} ($\Delta\nu_{OH}$) on adsorption.

In some systems (for example in the adsorption of VA and AN on AS/400), there is a change in the nature of the adsorption of the monomers at a coverage of about half an effective monolayer. In particular, at this degree of coverage there is a decrease in the heat of adsorption, the decrease being particularly marked for VA (~17 kJ mole^{-1}), a marked decrease in the width of the absorption bands in the ^1H NMR spectra of the adsorbates, and a displacement of the absorption band of the carbonyl groups of VA in the infrared spectra.[82]

The systems of the second group are characterised by localised activated adsorption, irreversible at room temperature.[56,73] In these systems the strength of the bonds between the monomer molecules and the surface is close to that of chemical bonds. These systems have been called systems "with strong bonding". Of the systems studied by the authors cited above, the following, in particular, are of this type: acrylic acid on an aminated aerosil, 4-vinylpyridine (4-VP) on a carboxylated aerosil, and 4-VP on an aerosil in the presence of water (in these, ionic bonds are formed). When 4-VP and N-vinylpyrrolidone (N-VP) are adsorbed on an aerosil, ionic bonds are not formed, but the stability of the adsorption complexes and the nature of the adsorption differ considerably from those for systems with weak bonding. Systems with strong bonding are characterised by values of the heats of adsorption of 100 to 200 kJ mole^{-1} and an extremely low surface mobility of the monomers.

The above separation of systems with strong and weak adsorption bonding is to some extent arbitrary. A particular system may "move" from one group to the other, for example when there is a marked change in the surface coverage or the temperature. The characteristics of a number of systems have intermediate values. Nevertheless, the proposed classification is useful, chiefly because of the marked differences in the nature of the processes of monomer polymerisation in the systems of the two groups.

The study of the processes involved in the surface molecular transport of monomers is of considerable interest. Here, the analysis of the possible influence of the surface diffusion of the monomers on the observed rate constant for the growth of the polymerisation chains is of fundamental importance. The coefficients of surface diffusion of the monomers D_s have been determined[56,73] for a number of systems with weak bonding (VA–AS/400, MMA–AS/200, MMA–AS/400, ST–AS/200, and VA–MAS). In these systems at temperatures of about 50 °C and degrees of covering of about one monolayer, $D_s = 10^{-5}$–10^{-3} cm^2 s^{-1}. The values of D_s increase rapidly with increase in temperature (the activation energy of surface diffusion decreases with increase in the concentration of adsorbed monomer σ). Within the monolayer, the values of D_s increase significantly with increase in σ, and in some systems (for example VA–MAS) they pass through a maximum.

Thus systems with weak bonding are characterised by high values of D_s for the monomers, close to the diffusion coefficients in non-viscous liquids. In systems with strong bonding, the values of D_s are much lower; for example, for 4-VP on an aerosil, $D_s = 10^{-8}$–10^{-9} cm^2 s^{-1}.

V. THE QUANTITATIVE STUDY OF THE ELEMENTARY STAGES OF RADICAL POLYMERISATION IN SYSTEMS WITH WEAK BONDING

An extremely important step in the determination of the characteristic features of polymerisation reactions on solid surfaces is the measurement of the rate constants for the elementary stages of these reactions. Considerable progress has been made in this field in the last few years. It has been possible to determine the rates of initiation v_i, the lifetimes of the kinetic chains τ, the growth rate constants k_g, and various other kinetic parameters of the radical polymerisation of a number of monomers on a silicon dioxide surface, initiated by radiation.[48,53–56,73]

Isolated attempts to estimate the growth rate constants for radiation polymerisation on a surface had been made earlier. The values of k_g had been calculated[50,51] for the grafted polymerisation of acrylonitrile on nylon fibre from the vapour phase using the post-effect. In these calculations the authors assume a "collision" mechanism of polymerisation, although in fact the mechanism is one of adsorption. Moreover, the estimation of the concentration of initiating radicals in the surface layer of the fibre was extremely arbitrary.

The authors cited concluded that the values of k_g on the surface are close to those observed in the radical polymerisation of AN in the liquid phase, and at the same time obtained for the activation energy of chain growth E_g a value of zero, which is unlikely for this reaction and which differs considerably from the values established for the radical polymerisation of AN and other monomers in the liquid phase. An attempt was made[81] to estimate the growth rate constant k_g for the radiation polymerisation of MMA on KSK-2 silica gel. The lifetimes of the kinetic chains were determined calorimetrically. In Ref. 81, the rate of initiation of the polymerisation was not determined experimentally;[81] it was assumed, somewhat arbitrarily, to be equal to the yield of paramagnetic centres stabilised in irradiated silica gel at 77 K, determined in Ref. 43. Moreover, it should be borne in mind that the yields of radicals in silica gels irradiated in the presence and absence of adsorbates usually differ considerably. They also depend on the concentration of impurities in the specimens. It was concluded[81] that k_g for MMA for monolayer coverage of the surface by the monomer is close to that for the liquid phase. For the above reasons, this conclusion does not appear completely reliable. The idea that k_g depends on the heat of adsorption and the degree of covering of the surface by the monomer was developed in Ref. 81.

The principal results[48,53–56,73] of the determination of the rate constants and other parameters of the elementary stages of the radiation polymerisation of VA and MMA on an aerosil and a methylated aerosil in the initial stage of the reaction can be considered.§ The kinetic parameters were determined using the usual equations of the theory of radical polymerisation which describe the stationary stage of the process:

$$\nu_{st} = \nu_i k_g [M] \tau$$

$$\nu_{t,sp} = 1/\tau;\ \nu_p = k_g [M] \tau;\ k_t = 1/\nu_i \tau^2 \qquad (2)$$

Here, ν_{st} is the stationary rate of polymerisation, $\nu_{t,sp}$ the specific (calculated for one growing chain) rate of termination, ν_p the length of the polymerisation kinetic chains, and k_t the rate constant for quadratic chain termination. The growth rate constants k_g were determined from Eqn. (2); here, the main difficulties are associated with the reliable measurement of the rates of polymerisation initiation ν_i and the lifetimes of the polymerisation kinetic chains τ.

1. Determination of the Rate of the Radiation Initiation of Polymerisation

As shown below, the initiation of radiation polymerisation on a surface when the concentrations of adsorbed monomers are not too high (up to 1–2 monolayers) is due chiefly to the active centres produced as a result of the absorption of the energy of the radiation by the solid. It should be noted that a sufficiently complete mechanism has not yet been reliably established for the radiolysis processes leading to the initiation of radical polymerisation on a surface, even for the most widely studied adsorbent silicon dioxide. It has been shown[35–38,84,85] by various methods (EPR, ultraviolet spectroscopy, etc.) that the γ-irradiation of finely dispersed silicon dioxide may lead to the production of hole, electronic, and radical centres on its surface. The hole centres may be localised on an oxygen atom of a hydroxide group or on an oxygen atom situated next to an impurity aluminium or boron atom.[36] Impurity atoms usually play an extremely important role in the localisation of electron or hole active centres and to a large extent determine the EPR and ultraviolet spectra of these centres. When an adsorbate is present on the surface of the irradiated specimens, transformation of these centres to radical-ions of the adsorbed molecules, or the formation of their donor–acceptor complexes with the adsorbate, is observed, depending on the relationship between the ionisation potential (or electron affinity) of the adsorbed molecules and the "depth" of the hole or electron traps. The radical-ions formed may take part in the initiation of surface ionic and radical reactions.

The initiation of radical reactions can also take place as a result of the transfer to the adsorbate molecules of the energy of recombination of the electron–hole pair, which is often sufficient for bond rupture in the adsorbed molecule. The energy of recombination of the ion pair may also bring about bond rupture in the surface silanol groups and the formation of $\geqslant SiO^{\bullet}$ and $\geqslant Si^{\bullet}$ radicals, and also the low-molecular-weight radicals $H^{\bullet}$ and $HO^{\bullet}$, which can also initiate radical reactions involving the adsorbate. It has been suggested[86,87] that an appreciable proportion of radical centres are formed by a homolytic mechanism.

The reliable determination of the rate of initiation of polymerisation ν_i on a surface is fairly complicated. The use of the usual methods for determining ν_i in the liquid phase, involving the measurement of the induction periods of inhibited polymerisation or the rate of consumption of radical acceptors,[89] in the case of polymerisation on a surface is complicated by the lowered diffusion mobility of the inhibitors and acceptors usually employed. As a result, their reactions with the active centres of the polymerisation are diffusion-controlled, and the efficiency of these reactions is lowered, making quantitative analysis of the results difficult.

Three different methods for determining ν_i, whose results show fairly good agreement with one another, have been developed and used: 1) the determination of the duration of the induction period of the polymerisation when an effective non-adsorbed inhibitor, namely gaseous oxygen, is used; 2) a kinetic method, based on the use of expressions, familiar from the theory of radical polymerisation, relating the average degree of polymerisation to the kinetic parameters of the process; and 3) a method based on the determination of the number of polymeric molecules formed in systems with a low effective constant for non-degenerate chain transfer. The characteristic features and limits of applicability of each method were discussed.[48]

Table 2 gives the values found by averaging the results obtained by different methods for ν_i and the radiation-chemical yields of the initiation calculated per unit of energy absorbed by the entire system G_i and by the adsorbed monomer G_i^* for the radiation polymerisation of MMA and VA on an aerosil. It is significant that the values of ν_i were found to be practically the same for the two monomers. Table 2 shows, in particular, that the values of G_i^* are anomalously high. This indicates directly that there is effective migration of the energy absorbed in the bulk of the aerosil particles to their surface. Table 2 also shows that the values of ν_i in the range of degrees of coverage from 0.4 to 1.5 monolayer depend little on the degree of coverage. In the temperature range studied, from −20 °C to +50 °C, the values of ν_i are practically independent of temperature.[48] The values of ν_i may differ significantly for a given monomer

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§See also M.A.Bruk, S.A.Pavlov, G.G.Isaeva, and E.Ya.Yunitskaya, Europ.Polym.J., 1986, 22, 169.

on different adsorbents. For example, the values of ν_i for VA on AS/400 and on MAS are ~10^7 molecule cm^{-2} s^{-1} and ~6×10^7 molecule cm^{-2} s^{-1} respectively.

Table 2. Average values of ν_i, G_i, and G_i^* for the radiation polymerisation of MMA and VA (dose rate 0.35 Gy s^{-1}).[48]

m *	10^{-7} ν_i, molecule $cm^{-2}s^{-1}$	G_i, 1/100 eV	G_i^*, 1/100 eV	m *	10^{-7} ν_i, molecule $cm^{-2}s^{-1}$	G_i, 1/100 eV	G_i^*, 1/100 eV
Adsorbent AS/400				Adsorbent AS/200			
0.4	1.1	1.0	30	0.4	1.3	1.2	47
1.0	1.2	1.1	17	1.0	1.4	1.3	20
1.5	1.3	1.2	12	1.5	1.6	1.5	15

*The number of effective monolayers of monomer on the surface in the polymerisation.

2. Determination of the Lifetimes and Rate Constants for the Growth of the Kinetic Chains

The lifetimes of the polymerisation kinetic chains τ have been determined from the measured durations of the initial non-stationary period of the polymerisation. Analysis of the relationship between τ and the extrapolated non-stationary time t_{ns} showed that for systems with linear termination of the kinetic chains $t_{ns} = \tau$,[56,83] and for systems with mixed termination $t_{ns} = z\tau$, where z lies in the range 0.7–1, depending on the ratio of the rates of linear and quadratic termination.[91] For systems with quadratic termination, $t_{ns} = \tau \ln 2$.[89] Thus in all cases, it is possible with sufficient accuracy to use the relationship $\tau \cong t_{ns}$.

The initial non-stationary stage of the polymerisation has been studied by two methods: vacuum gravimetry (VG) and adiabatic increase in temperature (AIT). The determination of t_{ns} by VG under real experimental conditions requires the introduction of a correction, associated chiefly with retardation in the diffusion transfer of the monomer in the specimen, and has a low accuracy.[56,73] The conclusion[83] that there is no diffusion retardation is apparently erroneous. The fact that the observed values of t_{ns} are independent of the thickness of the aerosil tablets on which the polymerisation was carried out, which provided the experimental basis for this conclusion, is probably related to the influence of the non-isothermal character of the specimen on the dynamics of the adsorption of the monomer.[56,73] Thus the values of k_g obtained in Ref.83 are several times too low.

The AIT method is more convenient for determining t_{ns}. The method involves essentially the measurement of the increase in the temperature of the specimen as a result of the heat liberated on polymerisation under pseudo-adiabatic conditions, when heat exchange between the specimen and the surrounding medium can be neglected. The measurements were made in a cell with an adiabaticity time from 5 min to 9 min; particular attention was paid to the analysis of the possible errors of the method.[56] The method used makes it possible to determine t_{ns} in the range 5 to 100 s with a relative error ≤30%. In Refs.53–56 the rate constants were calculated using the values of t_{ns} obtained by the AIT method.

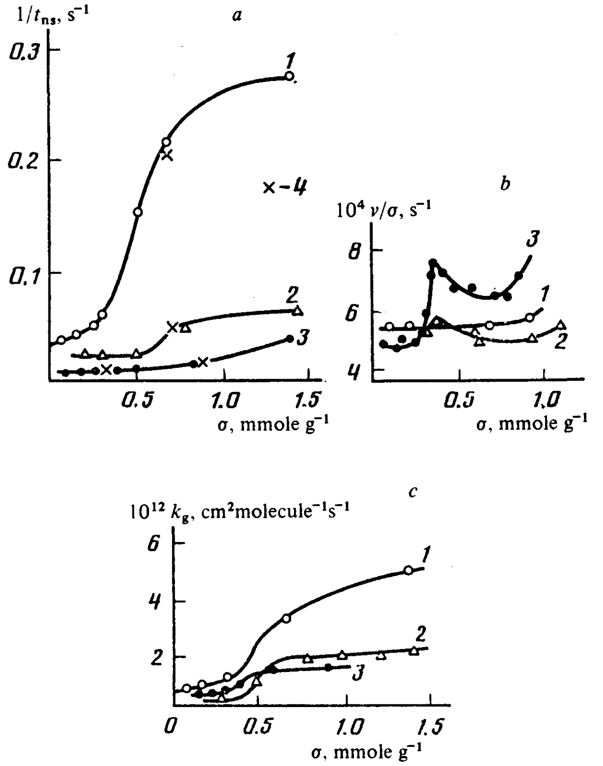

Figure 1. Dependence of $1/t_{ns}$ (*a*), the reduced stationary rate of polymerisation (*b*), and the chain growth rate constant (*c*) on the concentration of adsorbed monomer σ: *1*) VA on AS/400; *2*) MMA on AS/400; *3*) MMA on AS/200. Temperature 50 °C, dose rate 0.35 Gy s^{-1} (points *4* were obtained at 1.7 Gy s^{-1}).[9,55]

Fig.1*a* gives the results of the experimental determination of the values of $\nu_{t,sp} = 1/t_{ns}$ for various systems studied. The values of $\nu_{t,sp}$ are much lower than those for polymerisation in the liquid phase in the initial stages; these values increase with increase in the monomer concentration σ. These data, the values of ν_i given above, the values of ν_{st} given in Fig.1*b*, and Eqn.(2) were used to calculate the growth rate constants k_g for different values of σ. Fig.1*c* shows that the values of k_g are of the order of 10^{-12} cm^2 $molecule^{-1}$ s^{-1}, and that they increase with increase in σ. A significant feature is that k_g increases abruptly in the range of degrees of coverage corresponding to approximately half a monolayer (0.3–0.4 mmole g^{-1}), where an abrupt decrease in the heat of adsorption takes place (see section IV). Calculation shows that for VA molecules, which are adsorbed "more weakly" (filling the second half of an effective monolayer), the values of k_g on the average are ~4 times those for the monomer adsorbed "more strongly" (at degrees of covering of 0.2–0.3 monolayer).

Interesting results have been obtained in experiments on polymerisation in adsorbed solutions.[53,54] If two thirds of a monolayer of ethyl acetate (EA) are added to one third of a monolayer of VA, there is a sharp increase in the effective value of k_g (by a factor of ~4). It is suggested that this effect is related to the fact that in the presence of VA, whose adsorption properties on the aerosil are practically completely analogous to those of VA, an appreciable proportion of the VA molecules are displaced from strong to weak adsorption centres. When additives such as chloroform, which are adsorbed on the aerosil much more weakly than VA and EA, and which cannot displace the monomer from the strong centres, are introduced into the adsorption layer instead of EA, k_g remains practically unchanged.[54]

The question of whether the values of E_g are different for the monomer adsorbed on strong and weak centres are different is extremely important. Table 3 gives the results of a study of the temperature dependence of the rates of the overall process (E_{tot}), the termination reactions (E_t), and the growth (E_g) of the polymerisation chains of various monomers on AS/400 for different values of σ. As already noted, $E_i \cong 0$. It can be seen that E_g is much higher at low than at high degrees of covering. This difference corresponds approximately to the differences in k_g.

Table 3. Activation energies of the overall process (E_{tot}) and the reactions of chain growth (E_g) and termination (E_t) in the polymerisation of monomers on AS/400 (dose rate 0.35 Gy s^{-1}).[53,55]

Monomer	σ, mmole g^{-1}	Activation energies, kJ mole^{-1}		
		E_{tot}	E_t	E_g
VA	0.25	8.4	14.2	22.6
VA	0.7	6.3	10.9	17.2
MMA	0.25	28.5	9.7	38.2
MMA	0.65	21.8	9.7	31.5
MA	0.25	23.4	—	—
MA	0.7	10.5	—	—

Table 4. Kinetic parameters of the polymerisation of VA and MMA on an aerosil and on MAS (monolayer coverage, temperature 50 °C, dose rate 0.35 Gy s^{-1}).[9,55]

Parameter	VA-AS/400	VA-MAS	MMA-AS/400	MMA-AS/200
k_g, cm^{2}molecule^{-1}s^{-1}	$3.6\cdot10^{-12}$	$7.1\cdot10^{-13}$	$1.0\cdot10^{-12}$	$0.67\cdot10^{-12}$
k_t, cm^{2}molecule^{-1}s^{-1}	—	$2.4\cdot10^{-10}$	—	—
k_m, cm^{2}molecule^{-1}s^{-1}	$1.8\cdot10^{-15}$	—	$1.6\cdot10^{-17}$	$1.1\cdot10^{-17}$
10^{-8} n_{st}, cm^{-2}	0.72	4.9	3	8.4
10^{-3} $\bar{P}_n$	1.3	0.45	4	4.4
10^{-4} ν_p	0.44	1.2	0.5	0.8
τ, s	6	8.5	25	60

Notation: n_{st} is the stationary concentration of growing radicals; $\bar{P}_n$ the number-average degree of polymerisation; and k_m the rate constant for chain transfer to the monomer.

Table 4 gives the values of the principal kinetic parameters of polymerisation for some systems with weak bonding. Table 4 shows, in particular, that k_g for VA on MAS is ~2 times that on AS/400. This is apparently due to the weaker adsorption bonding of VA on the MAS surface.

3. Comparison of the Kinetic Parameters of Polymerisation on a Surface and in the Liquid Phase[9,55]

It is of considerable interest to compare the rate constants for the growth and termination of the chains in the polymerisation of monomers in the adsorbed state and in the liquid phase in the initial stages of the reaction (Table 5). The values of the surface constants were recalculated to the bulk values using a model in which the adsorbed monolayer is regarded as a reaction volume of thickness 4 Å, which is approximately equal to the gas-kinetic diameter of the monomer molecules. Table 5 shows, in particular, that the values of k_g, recalculated to bulk values, correlate well with the values of the specific rates of chain growth $\nu_{g,sp}$, which are independent of the concentration dimensions and are not related to the model adopted.¶ This indicates that the model adopted for the recalculation is correct.

Table 5. Kinetic parameters of the polymerisation of VA and MMA on the surface of AS/400 and MAS (monolayer coverage)[9,55] and in the liquid phase (in the bulk)[89,90] (temperature 50 °C).

Parameter	Vinyl acetate			Methyl methacrylate		
	on AS/400	on MAS	in the liquid phase	on AS/400	on AS/200	in the liquid phase
k_g, litre mole^{-1}s^{-1}	84	160	1500—2600	22	15.4	350—410
10^{19} k_g, cm^{3}molecule^{-1}s^{-1}	1.4	2.7	25—43	0.39	0.26	5.8—6.8
k_t, litre mole^{-1}s^{-1}	—	$5.4\cdot10^{3}$	$2{,}5\cdot10^{7}$	—	—	$2\cdot10^{7}$
10^{17} k_t, cm^{3}molecule^{-1}s^{-1}	—	0.9	$4.2\cdot10^{3}$	—	—	$3.3\cdot10^{3}$
$\nu_{g,st}$, s^{-1}	$0.73\cdot10^{3}$	$1.4\cdot10^{3}$	$(1.6—2.8)\cdot10^{4}$	$0.2\cdot10^{3}$	$0.15\cdot10^{3}$	$3.5\cdot10^{3}$
$\nu_{t,st}$, s^{-1}	0.16	0.12	—	0.04	0.017	1*

*For the radiation polymerisation of MMA in the bulk in the initial stage; dose rate 0.35 Gy s^{-1}.[32]

Table 5 shows that the rate constant of the quadratic termination k_t for the polymerisation of VA on MAS is lower by ~3.5 orders of magnitude than that in the liquid phase. This result is due to the diffusion character of k_t and the fact that the translational mobility of the macro-radicals on the surface is much lower than that in the liquid phase. The suppression of the quadratic termination of the chains on the surface is responsible for the low rates of termination and

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¶Thus Table 5 shows that the ratio of the bulk and surface specific growth rates for each of the systems studied is close to the ratio of the bulk and surface growth rate constants.

for the fact that the lifetimes of the polymerisation kinetic chains are much longer than those in the liquid phase. The same factor increases the role of linear chain termination in polymerisation on a surface and the occurrence of systems with linear and mixed termination. An analysis of the initial non-stationary stage in systems with mixed termination kinetics has been carried out.[91]

The data in Table 5 also show that for the systems studied, the values of k_g in an adsorbed monolayer are 15–20 times lower than those in the liquid phase.

The possible influence of processes of molecular transport of the monomers on the surface on the observed values of k_g has been analysed.[92] The analysis was carried out using the concepts of the theory of diffusion processes in an adsorbed layer, and also the experimentally determined values of D_s and data on the equilibrium adsorption of monomers. The authors obtained mathematical expressions which give the conditions for replacement of the limiting stage of the chain growth process (and also any other bimolecular reaction) on a surface, that is the conditions corresponding to the change from kinetic to diffusion conditions, and which make it possible to calculate the values of the effective rate constants of polymerisation under purely diffusion conditions and under intermediate conditions. The analysis showed that for values $D_s \cong 10^{-5}$ cm^2 s^{-1}, appreciable deviations of the concentration of the reagent close to the reaction centre from the equilibrium concentration for a bimolecular reaction on a surface are possible only for values of the chemical rate constant of this reaction greater than 10^{-6} cm^2 molecule^{-1} s^{-1}. This value corresponds to a bulk rate constant of ~10^{-13} cm^3 molecule^{-1} s^{-1} or 10^8 litre mole^{-1} s^{-1}; it is greater by ~5 orders of magnitude than the experimental values of k_g for the radical polymerisation of monomers in the liquid phase. Such high values of k_g obviously cannot be realised for non-catalytic reactions of radical polymerisation on a surface. Thus in the systems with weak bonding studied, as in the polymerisation of monomers in the liquid phase in the initial stages, kinetic conditions of chain growth are established.

With allowance for this, it is possible to examine the nature of the observed differences in the values of k_g on a surface (k_g^{surf}) and in the bulk (k_g^{bulk}). When examining the reactions of the chain growth of VA or MMA in an adsorbed monolayer on an aerosil, it is necessary to bear in mind that, according to adsorption measurements,[82] the monolayer can be regarded as a "compact" monolayer, in which the average area corresponding to one monomer molecule is close to the corresponding value for the liquid monomer. On the other hand, it is necessary to take account of the probable difference in the number of monomer molecules close to the reaction centre, in the reaction "cage" (n_c). The value of n_c is apparently 2–3 times lower for polymerisation in an adsorption monolayer than for polymerisation in the bulk of the liquid monomer. With allowance for this essentially concentration factor, however, the values of k_g^{surf} for the systems studied are appreciably lower than those for polymerisation in the bulk, by a factor of 6–8 for monolayer coverage, and by a factor of ~20 for a coverage corresponding to one third of a monolayer. These differences are due to corresponding differences in the nature of the elementary act of chain growth, related to the characteristic features of the structure of the intermediate complex and the form of the potential surface. A definite role may be played by both the energy and the entropy factors.[9,32,55] In the polymerisation of MMA, the energy factor, associated with the need for a decrease in the strength of the adsorption bond of the monomer, predominates; in the polymerisation of VA, a greater role is played by the entropy factor.

4. Various Thermodynamic Characteristics of Polymerisation on a Surface

The enthalpy and entropy of adsorbed monomers and polymers formed on a surface usually differ considerably from the corresponding parameters in the liquid and gas phases. Thus polymerisation on a surface should show definite thermodynamic characteristics. A general analysis of this question[32] leads to the conclusion that in polymerisation on a surface at degrees of covering up to one monolayer, the heat of polymerisation Q_{pol} may be appreciably lower (by ~10–50 kJ mole^{-1}) than that for the polymerisation of the corresponding monomers in the liquid phase. The examination of this question in Ref.1, where the opposite conclusion was reached, is apparently not completely correct (see Ref.32).

Various problems of the thermodynamics of polymerisation on a surface have been studied experimentally.[80,81] According to the results of a calorimetric study of the polymerisation of a number of monomers (AN, MMA, tetrafluoroethylene) adsorbed on KSK-2 silica gel, the effective heats of polymerisation $Q_{\text{pol}}^{\text{surf}}$ at low degrees of covering of the surface by the monomer differ considerably from the values of Q_{pol} for the polymerisation of the same monomers in the liquid phase. In some systems (for example for MMA and AN) at coverages of a quarter of a monolayer, the values of $Q_{\text{pol}}^{\text{surf}}$ are only 5–10 kJ mole^{-1}. With increase in the degree of covering of the surface, $Q_{\text{pol}}^{\text{surf}}$ increases (extremely sharply in the systems indicated), and in the range near one monolayer it reaches values characteristic of the liquid phase.

Some approximate thermodynamic estimates have also been made[32] using the results of a study of the polymerisation of VA and MMA on an AS/400 surface by the adiabatic increase in temperature method. These estimates showed that for both monomers, $Q_{\text{pol}}^{\text{surf}}$ increase considerably with increase in the degree of coverage of the surface by the monomers up to a monolayer, but at a coverage corresponding to a monolayer they still remain slightly lower than the values for the liquid phase; in the range of degrees of coverage studied, $Q_{\text{pol}}^{\text{surf}}$ for MMA is appreciably lower than that for VA.

VI. POLYMERISATION IN ADSORPTION POLY-LAYERS

The main regular features of polymerisation on a surface at comparatively low concentrations of the adsorbed monomers (up to 1–2 monolayers) were examined above. From the practical viewpoint, the examination of the characteristic features of polymerisation at higher monomer concentratons is also of considerable interest. These characteristics have been examined[93] for the radiation polymerisation of MMA and VA on AS/400. Specimens containing 50 mass % monomer relative to the aerosil were taken as model specimens with a "thick" adsorption layer. The layer thickness was ~10 to 15 effective monolayers. In the thick layer the order of the polymerisation reaction with respect to the dose rate is 0.8–0.85, whereas it is 1 in a monolayer, and 0.5 in the liquid phase. Thus in a thick adsorption layer, a mixed mechanism of chain termination, with linear termination predominating, is observed. The predominantly linear termination of the chains is confirmed by the weak dependence of the molecular mass of the PMMA, formed in the "thick" layer, on the radiation dose rate.

The dependence of the reduced rate of polymerisation (v/σ) on σ has been studied.[93] For both monomers (VA and MMA) this dependence shows extremal character with a maximum in the range of coverage corresponding to 3–4 monolayers (Fig. 2). The dependence of the molecular mass of PMMA on σ is similar. This is probably due to a corresponding change in the effective rate constants of growth (k_g^{eff}) and termination (k_t^{eff}); k_g^{eff} increases more rapidly at coverages up to 3–4 monolayers, and k_t^{eff} increases more rapidly at higher concentrations. Moreover, the reduced rate of initiation ν_i/σ decreases with increase in σ. For polymerisation in a model "thick" layer, the value of E_g^{eff} is close to E_g for the liquid phase. It is suggested that the constant k_g^{eff} for the "thick" layer is close to k_g for the liquid phase. The reaction of chain termination is specific, however; quadratic termination is suppressed to a considerable extent, and linear termination predominates. In the initial stages the value of $\nu_{t,sp}$ is appreciably lower than in the liquid phase. This is confirmed, in particular, by the fact that the molecular mass of PMMA formed by polymerisation in a "thick" layer is 6 times that for polymerisation in the bulk under comparable conditions.[93]

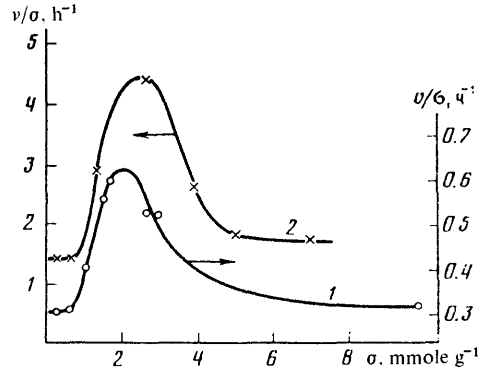

Figure 2. Dependence of the reduced rate of polymerisation ν/σ for VA (*1*) and MMA (*2*) on AS/400 on the concentration of adsorbed monomer σ. Temperature 50 °C, irradiation dose rate 0.1 Gy s^{-1} (*1*) and 0.35 Gy s^{-1} (*2*).[93]

The ratio of the rates of radiation polymerisation on a surface at different values of σ and in the bulk is illustrated by the data in Table 6 for MMA and n-butyl methacrylate (BMA) on an aerosil. Table 6 shows, in particular, that in the region of the maximum (at a coverage of ~4 monolayers), the reduced rate of polymerisation on the surface is 30 to 50 times that in the bulk under comparable conditions. An important feature is that this difference should increase with increase in the dose rate, because of the difference in the dependence of the reaction rate on the dose rate. These results are apparently typical of a fairly wide range of monomer–support systems. The main channels of this accelerating influence of the support on the polymerisation are: 1) increase in the rate of initiation of polymerisation, firstly because of the "maintenance" of the adsorption layer by the active centres formed by the energy of the radiation absorbed by the solid particles (this "maintenance" is particularly significant in those systems in which there is effective transfer of energy from the bulk to the surface of the particles), and secondly as a result of the increase in the radiation dose rate for the layer of monomer situated at the interface with the solid with a high electron density[88] (this effect is not very great for an aerosil, but it should be considerable for heavy metal oxides); 2) decrease in the probability of termination and increase in the lifetime of the polymerisation kinetic chains.

Table 6. Rates and radiation-chemical yields of the polymerisation and the molecular masses of the polymers of MMA and BMA, formed on an AS/400 surface and in the bulk (in the volume) [temperature 50° (MMA) and 25° (BMA), dose rate 0.35 Gy s^{-1}].[32,93]

Parameter	Monomer	Adsorbed state*			Liquid phase (in the bulk)
		1 monolayer	4 monolayers	"thick" layer	
10^4 (ν/σ), s^{-1}	MMA	4	12.5	6	0.4
	BMA	2.5	16	7	0.31
10^{-4} G_{pol}, 1/100 eV	MMA	0.61	6.5	6.0	0.94
	BMA	0.31	6.75	4.6	0.63
10^{-4} G_{pol}^*, 1/100 eV	MMA	10	31.2	18	0.94
	BMA	5	32.6	14	0.63
10^{-6} $\bar{M}_\eta$	MMA	0.6	4.8	2.9	0.5
	BMA	0.4	6.8	8.5	0.9

*Concentrations of adsorbed monomer for 1 monolayer, 4 monolayers, and the "thick" layer were 5 (? Ed. of trans.), 26, and 50 mass % respectively.

Various characteristics of radiation polymerisation in micron layers of monomers on solid surfaces† have been examined in general terms.[94] Attention is drawn to a possible change in the mechanism and rate of radiation-chemical transformations on a surface compared with polymerisation in the bulk. The "structure" of the monomer layer is examined with allowance for various characteristic features of the action of radiation on a heterogeneous system. In particular, a "range of molecular contact", which adjoins the support and in which higher rates of radiation polymerisation can be expected, is distinguished. The main factors responsible for this increase in the rate are considered[94] to be: 1) the increase in the dose rate in this range, due to the effect of radiation "reflected" from the solid; 2) the increased viscosity of the system, which hinders the termination of the growing radical chains; 3) the increase in the rate of chain growth, due to the ordered arrangement of the molecules relative to the substrate and one another. The effect of the first two factors appears indisputable. In the case of the last factor, however, the formation in the boundary layer on a solid surface of "prepared" monomer molecules whose relative arrangement would lead to an increase in the rate of polymerisation appears to be the exception rather than the rule. The formation of these "prepared" molecules requires at least strict complementarity between the support and the layer of adsorbed monomer.

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†That is in extremely thick (thousands of monolayers) adsorption layers or thin liquid films of the monomers.

VII. POLYMERISATION IN SYSTEMS WITH STRONG BONDING

For a number of reasons, the study of polymerisation in systems with strong bonding is usually associated with considerable experimental difficulties. There are very few published papers on these systems.

Acrylic acid chemisorbed on an aminated aerosil undergoes practically no polymerisation. The monomer adsorbed physically above the chemisorbed layer is polymerised at an extremely high rate.[56,73]

The polymerisation of N-vinylpyrrolidone on Silochrome[9,96] takes place practically only at temperatures above 70 °C. The rate of polymerisation and the molecular mass of the polymer formed are low. The total activation energy of the process is 60–70 kJ mole^{-2}. The order for the dependence of the rate of polymerisation on the dose rate is $n_i \cong 1$. A study of the combined polymerisation on Silochrome of N-VP and the weakly-bonded monomer methacrylic acid gave an interesting result. At all compositions of the original mixtures studied, including mixtures containing 95 mole % N-VP, only pure polymethacrylic acid is formed, although the constants for the copolymerisation of these monomers in the liquid phase are similar. This shows that increase in the strength of the adsorption bonding decreases the effective reactivity of the monomer on the surface.

4-Vinylpyridine on AS/400 at 20–50 °C is polymerised at a rate which is 5–10 times lower than that for, for example, MMA under comparable experimental conditions. The molecular masses of the poly-4-VP formed are much lower.[9,73]

Thus the rates of polymerisation and the molecular masses of the polymers formed in typical systems with strong bonding are much lower than those in systems with weak bonding. These characteristic features are probably due chiefly to the much lower values of the effective growth rate constants. The values of k_g in systems with strong bonding are apparently 2–3 or more orders of magnitude lower than those for the polymerisation of the corresponding monomers in the liquid phase.

The polymerisation of 2-methyl-5-vinylpyridine on silica gel at high temperatures (90–150 °C) has been studied.[97] Under these conditions the rate of the process is fairly high. Judging from the kinetic data,[97] $G_{\text{pol}} \cong 10^4$ at 100 °C. At high temperatures this system apparently behaves like a typical system with weak bonding (see section IV).

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Thus in recent years considerable progress has been made in the study of the mechanism and characteristic features of the elementary stages of radiation polymerisation on a surface, providing a basis for the development of the theory of these reactions. Nevertheless, many unresolved problems remain in this field, primarily those related to the mechanism of the elementary stages of these processes. In the case of the initiation stage, it is necessary to study the influence of the electronic character, the actual structure, and the particle size of the solid on the rate of initiation and to determine the mechanism of the basic radiation reactions leading to the formation of the initiating centres. The more accurate determination of the conditions under which the surface exerts stereochemical control over the acts of chain growth is of particular interest; in this connection it is appropriate to study the characteristic features of the micro-structure of the polymer chains obtained in systems with strong adsorption bonding. Finally, it is necessary to carry out additional studies of the detailed mechanisms of linear and quadratic chain termination in real systems, including adsorption layers of different thickness. The study of this question should give new results of fundamental importance, related to the properties of the macromolecules and their solutions on solid surfaces. It is also extremely important to extend the range of systems in which the kinetic parameters of polymerisation are determined, to make detailed studies of the processes of ionic radiation polymerisation on a surface, and to study the characteristic features of polymerisation on regular supports and of oriented and matrix polymerisation on a surface.

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Halogenodeoxy-derivatives of Cellulose

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Halogenodeoxy-derivatives of cellulose are examined for the first time in terms of a wide range of their characteristics: synthesis, methods for the determination of structure, reactions, and properties. The replacement of some of the hydroxy-groups of cellulose by halogen atoms imparts to it a number of practically important properties, for example resistance to combustion and acid or enzyme hydrolysis. The reactive halogenodeoxy-derivatives of cellulose are used for the synthesis of a wide variety of cellulose derivatives with functional groups, frequently with properties of practical interest. The bibliography includes 70 references.

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I. INTRODUCTION

Cellulose is a unique organic compound: it is available in large amounts and it is being continuously renewed. The introduction of a halogen into the glucopyranose unit of cellulose as well as the reactions of halogenodeoxycelluloses can be used to synthesise new materials with properties specified beforehand.

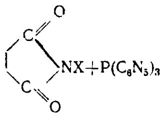
Halogenodeoxy-derivatives of cellulose have not been considered in the reviews devoted to the chemistry of halogenodeoxy-derivatives of monosaccharides.[1,2] In the monographs on cellulose chemistry, the derivatives of this class are either not considered[3,4] or their treatment is incomplete.[5,6]

Since the earlier review by the present author and Golova,[7] devoted to the synthesis and properties of various deoxycelluloses, including halogenodeoxy-derivatives, was written, methods of their synthesis known previously have been significantly developed, new methods have appeared, new procedures for the determination of their structure have been developed, and some of their properties have been investigated in greater depth.

II. METHODS OF SYNTHESIS

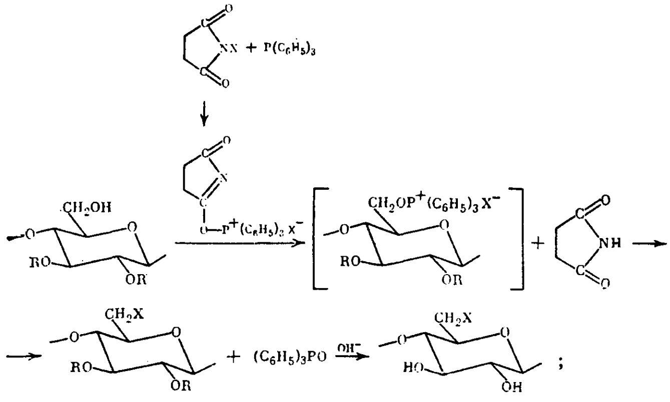
The studies in the synthesis of halogenodeoxycelluloses have developed in several directions, including procedures for the most complete substitution of all the hydroxy-groups of cellulose by halogen atoms,[8] the utilisation of the possibilities for the selective introduction of a halogen at specific carbon atoms of the glucopyranose unit of cellulose,[9-13] the development of methods for the introduction of a halogen into the cellulose macromolecule which are already known,[9,14,15] and the search for new cellulose halogenating agents, for example *N*-halogenosuccinimides,[9,10] SO_2Cl_2,[11,12] SF_4,[16-18] etc. Methods for the substitution of the relatively unreactive secondary hydroxy-groups of cellulose by a halogen are being developed[11,14,15] and a search is being prosecuted for reagents which would make it possible to introduce various halogens into the cellulose macromolecule under comparable conditions; the latter is associated with the fact that various halogenodeoxycelluloses, obtained under identical conditions, should have more similar physicochemical properties than the analogous derivatives obtained by different methods, which is extremely important for the subsequent comparative study of their properties.[9,10] The behaviour of a number of partly substituted cellulose derivatives under conditions where the free hydroxy-groups are substituted by a halogen is also being investigated;[19,20,38] in particular, the stability of various blocking groups, the removal of blocking groups in the presence of a halogen, and problems associated with the preparation (activation) of cellulose before halogenation reactions are being studied.[13,21] These and other problems have been solved to a greater or lesser extent in recent years. The principal reactions and reagents employed for the synthesis of halogenodeoxycelluloses are listed in Table 1.

Table 1. The reactions and reagents used to synthesise halogenodeoxycellulose.

Reaction, initial cellulose derivative, type of reagent	Reagent	Refs.
Nucleophilic substitution of a cellulose OH group on treatment with acid chlorides	SO_2Cl_2 $SOCl_2$ $POCl_3$ RSO_2Cl	[11, 12] [8.14, 19—25] [26] [13,27,28]
Nucleophilic substitution by means of metal halides of active functional groups introduced into cellulose beforehand	MX(X=Cl, Br, I, F)	[14,15,20, 29—34]
alkane- and arene-sulphonate	—	[34]
sulphate	—	[34—37]
nitrate	—	
phosphinite with alkyl halide	RCl	[38]
Nucleophilic substitution of a cellulose OH group by reaction with halogen-containing phosphorus compounds	 $NX+P(C_6N_5)_3$ X=Cl, Br, I	[9,10]
	$CH_3I\cdot P(OC_6H_5)_3$	[19,39,40]
	Cl_2 or Br_2+P	[41]
Nucleophilic substitution of cellulose OH groups by reaction with halogen-containing sulphur compounds	SF_4	[16—18]
Addition of hydrogen halide to 2,3-epoxy-derivative of cellulose	HCl	[42]
Addition of a halogen to 5,6-cellulosene	Cl_2, Br_2	[43]

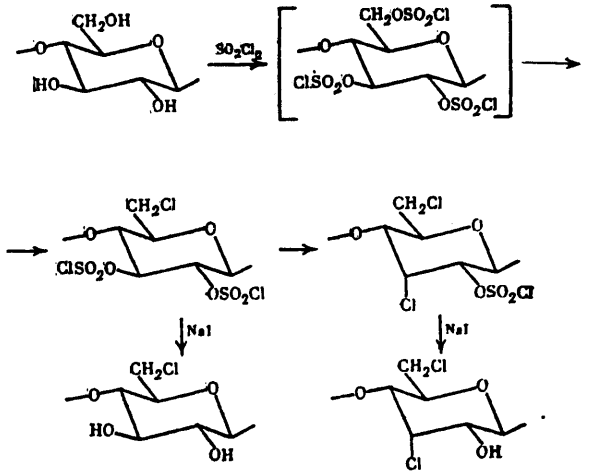
A new convenient method of synthesis of 6-chloro-, 6-bromo-, and 6-iodo-6-deoxycelluloses under comparable conditions involves the reaction of partly substituted

2,3-di-O-acetylcellulose with the *N*-halogenosuccinimide and triphenylphosphine with subsequent deacetylation.[9,10] 2,3-Di-O-acetylcellulose is initially dissolved in dimethylformamide (DMF) and is then treated with the reagent for 5 h at 50 °C with a glucopyranose unit : *N*-halogenosuccinimide : triphenylphosphine ratio of 1 : 2 : 2 in order to obtain the chloro- and bromo-derivatives and 1 : 6 : 6 in order to obtain iododeoxycellulose. Under identical conditions, *N*-iodosuccinimide proved to be the least reactive. There are virtually no side reactions in the case of *N*-chloro- and *N*-bromo-succinimides. After the first hour, the reaction slows down sharply and the degree of substitution (D.S.) reaches a limit corresponding to the substitution by the halogen of one (or approximately one) hydroxy-group in the glucopyranose unit. Under the reaction conditions, the acetyl groups are retained but can be fully removed from halogenodeoxycelluloses by treatment with a 0.25 *N* NaOH solution for 1 h. This results in the formation of 6-chloro- and 6-iodo-6-deoxycelluloses in 83–95% yield under mild conditions with D.S. = 1.0, 0.8, and 0.7 respectively.



R=H, Ac; X=Cl, Br, I .

The mildest and most effective reagent for the substitution of the hydroxy-groups of cellulose by chlorine is sulphuryl chloride.[11,12] A suspension of cellulose in chloroform is treated with sulphuryl chloride in the presence of pyridine using the molar ratios OH : SO_2Cl_2 : Py = 1 : 1.7–5 : 1–8 during a period ranging from 20 min to 3 h. The reaction takes place at room temperature and does not require the preliminary dissolution of cellulose. A chlorosulphate derivative of cellulose is apparently formed as an intermediate. The reaction product contains, together with the chlorodeoxy-groups, also the chlorosulphate groups, which are resistant to substitution by halogen and sulphate groups. The chlorosulphate groups can be removed quantitatively by treating the polymer with sodium iodide in aqueous methanol and the sulphate groups can be eliminated by successive treatment with a base and an acid. This results in the formation of chlorodeoxycellulose containing 12.4 to 30.4% of chlorine (D.S. up to 1.7) and 1.2–0.9% of sulphur. The primary hydroxy-groups are exchanged for chlorine in the first place and then the secondary hydroxy-groups are exchanged. The substitution of a secondary hydroxy-group by chlorine atoms is accompanied by the inversion of the configuration. A distinctive feature of the reagent is its high selectivity: among the secondary hydroxy-groups, only the hydroxy-group in the C(3)-position is substituted by chlorine. The hydroxy-group at C(2) remains unsubstituted.



Highly chlorinated cellulose with D.S. = 2.8 has been obtained by treating cellulose with thionyl chloride in solution.[8] Cellulose is dissolved in 50–100 parts of DMF in the presence of 10 parts of chloral at 40 °C for 15 h and is treated with 15–30 parts of thionyl chloride at 20 °C for 15 h or at 40° and 80 °C for 1 h. The product contains 46–47.3% of chlorine and 2% of sulphur.

$$C_6H_7O_2(OH)_3 \xrightarrow{CCl_3CHO} C_6H_7O_2[OCH(OH)CCl_3]_3 \xrightarrow{SOCl_2} C_6H_7O_2(OH)_{0,2}Cl_{2,8} .$$

The reaction of cellulose with thionyl chloride is one of the principal reactions used for the synthesis of chlorodeoxycellulose. It has frequently attracted the attention of investigators[8,14,19–25] and its conditions have been most thoroughly investigated compared with other reactions. The principal results are compiled in Table 2.

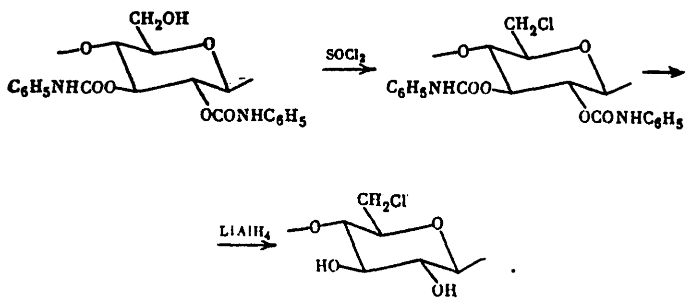
Table 2. Reactions of cellulose and its derivatives with thionyl chloride.

Reaction conditions			D.S.	Refs.
solvent	temperature, °C	time, h		
Pyridine	110	—	1	[21]
Pyridine	26—69	1.5	1	[22]
DMF	60—98	1—1.5	1.09	[23]
DMF	20	4	0.3	[24]
$CHCl_3$, CCl_4	B.p.	1—210	0.9	[25]
DMF + CCl_3CHO	20—80	1—15	2.8	[8]
DMF	70	0.4*	1	[19.20]
DMF	70	1.5—6**	0.47	[19]
HMP***	70	3**	0.75	[14.20]

*On a cellulose derivative with a free primary OH group.
**On cellulose derivatives with free secondary OH groups.
***HMP = hexamethylphosphoramide.

In order to introduce chlorine in a specific position in the glucopyranose cellulose unit, thionyl chloride in DMF is allowed to react with partly substituted cellulose derivatives: 2,3-di-O-phenylcarbamoylcellulose, 6-O-trityl-2(3)-tosylcellulose, 2(3),6-di-O-tosylcellulose, and 6-O-phenylcarbamoyl-2(3)-tosylcellulose.[19,20] It has been shown that the primary hydroxy-group in 2,3-di-O-phenylcarbamoylcellulose is fully substituted by chlorine already in the course of the first

15 min of the reaction (70 °C, tenfold excess of the reagent).[19] The phenylcarbamate groups can be removed by treatment with lithium tetrahydroaluminate in tetrahydrofuran (THF) for 1 h at 70 °C with the preferential retention of chlorine.[20]



The free secondary hydroxy-groups in the partly substituted 6(2,3)-O-phenylcarbamoyl-2(3)-O-tosylcellulose are much less reactive. Under the same conditions, they are substituted to the extent of only 20% after 1.5 h of the reaction and, when the reaction time is raised from 1.5 to 6 h, the degree of substitution is 50%. The nitrogen and sulphur contents in the products indicate the retention of the blocking phenylcarbamate and tosylate groups under the reaction conditions. On increasing the reaction time to 12 h, partial removal of the phenylcarbamate groups is observed.[19]

The free hydroxy-groups in the tosylated cellulose 6(2,3)-phenylcarbamate can be fully substituted by chlorine on treatment with thionyl chloride using hexamethylphosphoramide (HMP) as the solvent.[14,20] After 1.5 h of the reaction in HMP, the hydroxy-groups are replaced by chlorine to the extent of 70% and after 3 h their substitution is complete. The contents of sulphur and nitrogen in the final product indicate the retention of the tosylate and phenylcarbamate groups under the reaction conditions: the degree of substitution is 1.55 for the $OCONHC_6H_5$ groups, 0.7 for the OTs groups, and 0.75 for Cl atoms. The use of HMP as the solvent increases the rate of reaction of the hydroxy-groups of cellulose with thionyl chloride and also the degree of their substitution by chlorine.[14]

The reaction involving the substitution of active functional groups (alkane- and arene-sulphonate groups, nitro-groups, etc.), introduced into cellulose beforehand, by a halogen atom by treatment with alkali metal halides constitutes a widely used method for the halogenation of cellulose:[14,15,20, 29–37]

$$C_6H_7O_2(OH)_{3-n}(OR)_n \xrightarrow{MX} C_6H_7O_2(OH)_{3-n}(OR)_{n-m}X_m$$
$$R{=}SO_2R',\ SO_2OH,\ NO_2;$$
$$R'{=}CH_3,\ C_2H_5,\ C_6H_5,\ C_7H_7,\ C_6H_4NO_2,\ C_6H_4Br;$$
$$X{=}Cl,\ Br,\ I,\ F\ .$$

The principal results of the use of this reaction for the halogenation of cellulose and its derivatives are presented in Table 3.

The possibility of substituting the secondary hydroxy-groups in cellulose by halogen atoms via the reactions of cellulose alkane- and arene-sulphonates with alkali metal halides has been investigated. The trityl ether of cellulose is esterified by the chlorides of methane-, ethane-, benzene-, toluene-, p-bromobenzene-, and p-nitrobenzene-sulphonic acids and is then treated with NaI at 100 °C for 10–100 h.[15] Tritylcellulose p-nitrobenzenesulphonate is the most reactive. When this ester, having D.S. = 0.91 with respect to the $OSO_2C_6H_4NO_2$ groups, is iodinated for 100 h at 120 °C, a product with D.S. = 0.52 with respect to I is obtained, while the remaining esters give rise to products with D.S. = 0.25 with respect to I.

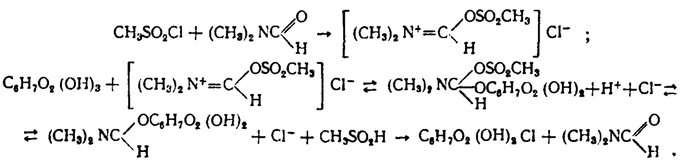
The use of HMP as the solvent makes it possible to substitute 60–80% of the secondary tosyloxy-groups in tritylcellulose tosylate on treatment with LiCl. The chlorine content in the final product corresonds to D.S. = 0.65–0.72.[14,20]

Table 3. The reactions of cellulose alkane- and arene-sulphonates, sulphates, and nitrates with alkali metal halides.

Reaction conditions			D.S.	Refs.
solvent	temperature, °C	time, h		
Acetone	100	2	0.2	[29]
Cyclohexanone	120	2	0.2	[30]
Acetylacetone	120	0.5—6	0.95—1.2	[31]
H_2O	—	—	—	[32]
DMF	97	24	0.9—1.22	[33]
H_2O	108—130	1—35	0.2—0.4	[34]
DMF	100—140	16—50	0.3—0.5*	[15]
HMP	97	10	0.65—0.72*	[14,20]

*Substitution of secondary arene- and alkane-sulphonyloxy-groups in 6-O-tritylcellulose esters.

The reaction with methanesulphonyl chloride has been proposed recently for the preparation of chlorodeoxycelluloses.[13,27] Chlorodeoxycellulose with D.S. = 0.58 is obtained by treating cotton cellulose activated with alkali or acetylcellulose in DMF with methanesulphonyl chloride.[27] The reaction mechanism involving the formation of an intermediate iminium derivative has been proposed[27] on the basis of the data of Edwards et al.:[44]



$$CH_3SO_2Cl + (CH_3)_2NC{\lesssim}^{O}_{H} \rightarrow \left[(CH_3)_2N^+{=}C{<}^{OSO_2CH_3}_{H}\right]Cl^- \ ;$$
$$C_6H_7O_2(OH)_3 + \left[(CH_3)_2N^+{=}C{<}^{OSO_2CH_3}_{H}\right]Cl^- \rightleftarrows (CH_3)_2NC{\overset{OSO_2CH_3}{\underset{H}{\leftarrow}}}OC_6H_7O_2(OH)_2 + H^+ + Cl^- \rightleftarrows$$
$$\rightleftarrows (CH_3)_2NC{<}^{OC_6H_7O_2(OH)_2}_{H} + Cl^- + CH_3SO_2H \rightarrow C_6H_7O_2(OH)_2Cl + (CH_3)_2NC{\lesssim}^{O}_{H}\ .$$

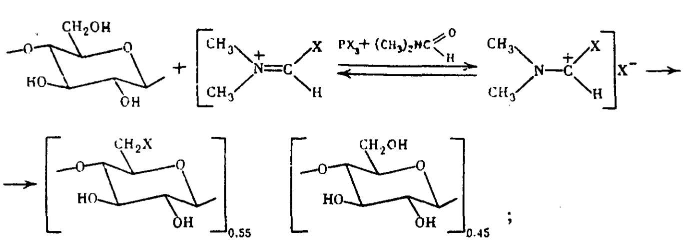
The higher D.S. = 0.83 in the reaction with methanesulphonyl chloride is attained when cellulose regenerated from its solution in cupriethylenediamine by precipitation in DMF is employed.[13] It has been noted that the effectiveness of the reaction is higher when it is carried out at 90 °C for a shorter time than at 60 °C for a longer time. A side reaction involving the introduction of formyl groups into cellulose is observed. They are removed by keeping the reaction product in an aqueous solution of sodium carbonate at room temperature.

Chlorodeoxycellulose with D.S. = 1.3 has been obtained by this reaction by dissolving cellulose in the DMF–chloral system (in the course of a week at room temperature) and subsequent treatment with methanesulphonyl chloride at 75 °C.[28] The chlorine content in cellulose reaches 16% after 1 h of the reaction and 24% after 48 h.

$$C_6H_7O_2(OH)_3 \xrightarrow{CCl_3CHO} C_6H_7O_2[OCH(OH)CCl_3]_3 \xrightarrow{CH_3SO_2Cl} C_6H_7O_2(OH)_{1,7}Cl_{1,3}\ .$$

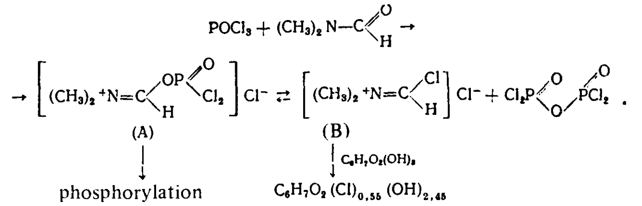
Extensive substitution of the secondary hydroxy-groups of cellulose by chlorine on interaction of tritylcellulose with alkane- and arene-sulphonyl chlorides, especially ethanesulphonyl chloride, has been reported.[15] With increase of reaction time from 24 to 72 h, the D.S. increases from 0.5 to 0.7.

Among other methods, mention should be made of the reaction of cellulose with halogen-containing phosphorus derivatives. Thus the hydroxy-groups of cellulose have been substituted by halogen on treatment with bromine or chlorine in the presence of phosphorus.[41] The reaction is carried out in DMF. The synthesis of bromodeoxycellulose by this reaction has been studied in greatest detail. A temperature of 50–70 °C and glucopyranose unit : phosphorous : bromine molar ratios of 1 : 1 : 30 are optimum for the maximum introduction of bromine. The bromodeoxycellulose obtained under these conditions contains 16% of bromine. The formation of cellulose phosphates in side reactions (phosphorus content 1.5%) and the appearance of carbonyl groups (an absorption band occurs in the IR spectrum at 1693 cm^{-1}) have been noted. When chlorine was passed through the reaction mixture under the same conditions at 60 °C for 6 h, chlorodeoxycellulose containing 10.2% of chlorine and 1.4% of phosphorus was obtained.



X = Cl, Br .

When cellulose is treated with phosphoryl chloride in DMF, chlorodeoxycellulose or phosphorylated cellulose is obtained depending on the reaction conditions.[26] The mode of reaction depends to a large extent on the reagent concentration and this dependence is maintained over a wide temperature range. It has been found that the following conditions are optimal for the synthesis of chlorodeoxycellulose: concentration of phosphoryl chloride in DMF 12%, temperature 75 °C, time 1 h. D.S. = 0.55 is attainable. On the basis of literature data,[45,46] the intermediate formation of active compounds (A) and (B)has been postulated:[26]



$$POCl_3 + (CH_3)_2N{-}CHO \rightarrow \left[(CH_3)_2{}^+N{=}CH{-}OP(O)Cl_2\right]Cl^- \rightleftarrows \left[(CH_3)_2{}^+N{=}CHCl\right]Cl^- + Cl_2P(O){-}O{-}P(O)Cl_2\ .$$

(A) → phosphorylation

(B) $\xrightarrow{C_6H_7O_2(OH)_3} C_6H_7O_2(Cl)_{0,55}(OH)_{2,45}$

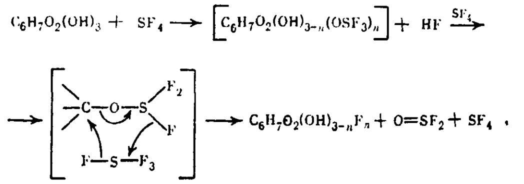
At a high phosphoryl chloride concentration, the interaction of cellulose with compound (B) leads to the formation of chlorodeoxycellulose. It had been shown earlier[47] that compound (B) plays an important role in the formation of chlorodeoxycellulose.

The reaction involving the substitution of the hydroxy-groups of cellulose by iodine on treatment of the following cellulose derivatives with triphenoxymethylphosphonium iodide has been investigated: tritylcellulose,[19,39,40] 2,3-di-*O*-phenylcarbamoylcellulose, and 2(3),6-di-*O*-tosylcellulose.[19,39] A possible reaction mechanism has been proposed.[48]

$$CH_3I + P(OC_6H_5)_3 \rightarrow [CH_3P^+(OC_6H_5)_3]\,I^- \xrightarrow{C_6H_7O_2(OR)_n(OH)_{3-n}}$$
$$\rightarrow \{C_6H_7O_2(OR)_n(OH)_{3-n-m}[OP^+(CH_3)(OC_6H_5)_2]_m\}\,I^- + C_6H_5OH \rightarrow$$
$$\rightarrow C_6H_7O_2(OR)_n(OH)_{3-n-m}I_m + CH_3PO(OC_6H_5)_2\ ;$$
$$R{=}OTr,\ OCONHPh\ .$$

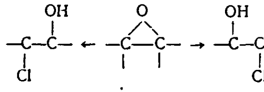
The products of the reaction with tritylcellulose were found to contain 15.2% of iodine after 3 h, 16.1% after 5 h, and 12.25% after 10 h.[19,39] It has been shown[40] that, when tritylcellulose is acted upon by the complex of triphenyl phosphite with an alkyl halide at a temperature below 60 °C, the substitution of hydroxy-groups by iodine is not observed. An increase of temperature from 60° to 120 °C leads to an appreciable increase of D.S. with respect to iodine (from 0.25 to 0.98). When the reaction of 2,3-di-*O*-phenylcarbamoylcellulose with triphenoxymethylphosphonium iodide is carried out in chloroform with a glucopyranose unit: halogenating complex molar ratio of 1 : 15 and a reaction time of 10–40 h at 60–120 °C, the maximum iodine content in the product is 11.6% (D.S. = 0.4).[19,39] Despite the fact that the reaction of 2(3),6-di-*O*-tosylcellulose with triphenoxymethylphosphonium iodide in chloroform takes place under homogeneous conditions, the D.S. with respect to iodine remains low (0.42). The reduced sulphur content indicates a decrease in the number of blocking tosylate groups under these conditions.[19,39]

Fluorodeoxycellulose with a high degree of substitution has been obtained by the reaction of cellulose with SF$_4$.[16,17,18] The degree of fluorination depends on the ratio of the initial components and the reaction time. With increase of the sulphur tetrafluoride: glucopyranose unit molar ratio, the rate of reaction and the content of the fluorine introduced into cellulose increase. The maximum amount of fluorine was introduced on treatment of the glucopyranose unit with a 30-fold molar excess of SF$_4$ for 6 h. The fluorodeoxycellulose with D.S. = 1.5 obtained was characterised by elemental analysis and IR spectra.[16–18] The substitution of hydroxy-groups by fluorine can take place without the inversion of configuration via the mechanism[49]



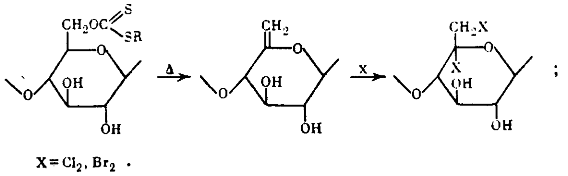
$$C_6H_7O_2(OH)_3 + SF_4 \longrightarrow \left[C_6H_7O_2(OH)_{3-n}(OSF_3)_n\right] + HF \xrightarrow{SF_4}$$
$$\longrightarrow [\ \ ] \longrightarrow C_6H_7O_2(OH)_{3-n}F_n + O{=}SF_2 + SF_4\ .$$

When the trityl group was split off from the 6-*O*-trityl-2,3-anhydro-derivative of cellulose with a solution of hydrochloric acid in methanol or chloroform for 24 h at room temperature, products with D.S. = 0.2–0.4 with respect to chlorine were obtained.[42] The authors suggested the formation of 2-chloro-2-deoxyglucose and 3-chloro-3-deoxyaltrose units:



$$-\underset{Cl}{C}-\overset{OH}{C}- \leftarrow -C\overset{O}{-}C- \rightarrow -\overset{OH}{C}-\underset{Cl}{C}-$$

The introduction of a halogen into the cellulose macromolecule can be achieved via a reaction involving the addition of the halogen to the double bonds in 5,6-cellulosene.[43] 5,6-Cellulosene is obtained by the pyrolysis of cellulose 6-(alkylxanthate) at 170 °C in a stream of argon. Cellulose derivatives containing 17.5% of bromine or 8.5% of chlorine have been obtained by treating a solution of 5,6-cellulosene in carbon tetrachloride with Br$_2$ and Cl$_2$ at room temperature for 3 h. The reaction products were characterised by elemental analysis and IR spectra:



X = Cl$_2$, Br$_2$.

III. METHODS FOR THE DETERMINATION OF STRUCTURE

The determination of the structure of halogeneodeoxycelluloses is essential for the solution of two interrelated problems: on the one hand, for the identification of a newly synthesised derivative and, on the other, for the elucidation of the transformations which cellulose undergoes under the conditions of a particular reaction. The question of the determination of the structure is the most complex: (1) on partial substitution of hydroxy-groups; (2) on non-selective substitution of three different hydroxy-groups of the glucopyranose unit of cellulose; (3) on inversion of the configuration in the reaction centre whereupon the secondary hydroxy-groups enter into the reaction; (4) when secondary reactions occur. The macromolecule of the cellulose derivative can contain in the general case, together with the unchanged glucopyranose units, also a series of glucopyranose units differing in the degree of substitution, the position of the substituent, and the stereochemistry of their reaction centres, as well as monosaccharide units formed as a result of side reactions. The determination of the structure of cellulose derivatives therefore involves the solution of two problems: (1) the determination of the monosaccharide composition, which entails the elucidation, in its turn, of problems such as that of the degree of substitution, the position of the substituent in the glucopyranose unit, and the configuration of the substituent; (2) the determination of the squence in which the monosaccharide residues are linked up in the macromolecule.

Until recently, there were no reliable methods for the investigation of the structure of halogenodeoxycelluloses. Due to the general development of the methods for the determination of the structure of carbohydrates and their derivatives and also in connection with the advances in the research into the reactions of halogenodeoxycelluloses, such methods have now been developed.

In order to establish the structure of halogenodeoxycelluloses, methods which both cause and do not cause the degradation of the polysaccharide chain are used. The former include acid hydrolysis in combination with paper—thin-layer—(TLC) or gas—liquid (GLC) chromatography together with chromatomass-spectrometric, and spectrophotometric methods for the investigation of the hydrolysates. Among the non-degradative methods, chemical methods based on selective reactions with the primary hydroxy-group (tosylation with subsequent iodination), and the glycol group (periodate oxidation), as well as spectroscopic methods (^{13}C NMR) are used for the determination of the structure of halogenodeoxycelluloses.

Quantitative analysis of the monosaccharide composition of 6-bromo- and 6-iodo-6-deoxy-celluloses has become possible since a procedure has been found for their quantitative reduction to 6-deoxycellulose.[9,10] In contrast to halogenodeoxycelluloses, the latter does not undergo side reactions during the hydrolysis of the polysaccharide, the tetrahydroborate reduction, and acetylation and can be investigated by the usual methods for the structural analysis of polysaccharides. The position of the halogen in the bromo- and iodo-deoxycelluloses obtained by reaction with *N*-halogenosuccinimide and triphenylphosphine has been rigorously demonstrated by this method.[9,10] The amount of 6-deoxyglucose found by GLC and spectrophotometric methods in the reduced specimens of bromo- and iodo-deoxycelluloses corresponds to the halogen content in the halogenodeoxycelluloses investigated. This demonstrates unambiguously that the entire bromine and iodine introduced into cellulose is located at the six carbon atom of the glucopyranose unit of cellulose.[9,10]

Chlorodeoxycellulose is only partly reduced by $NaBH_4$. Apart from 6-deoxyglucose and glucose, 6-chloro-6-deoxyglucose and 3,6-anhydroglucose were detected in the hydrolysis products after the reduction of chlorodeoxycellulose. Owing to the instability of these compounds under the hydrolysis conditions, it is impossible to carry out a complete quantitative analysis of the monosaccharide composition of the polymer using the hydrolytic and chromatographic methods.

A convenient procedure for the determination of the structure of chlorodeoxycelluloses is ^{13}C NMR.[12,50] The characteristics of the changes in the chemical shifts of the signals due to the carbon atoms on substitution of the hydroxy-groups by chlorine atoms in both the given and neighbouring monosaccharide units in the disaccharides investigated have been established for the model compounds β-methyl cellobioside, methyl 6,6′-dichloro-6,6′dideoxycellobioside, methyl (3′,6′-dichloro-3′,6′-dideoxyallopyranosyl)-6-chloro-6-deoxyglucopyranoside, and methyl (3′,6′dichloro-3′,6′-dideoxyallopyranosyl)-3,6-dichloro-3,6-dideoxyallopyranoside.[50] The chemical shifts of the C(1) signals have been calculated on the basis of the spectra of the test compounds for all the possible sequences in which the monosaccharide derivatives comprising unsubstituted D-glucose, 6-chloro-6-deoxy-D-glucopyranose, and 3,6-di-chloro-3,6-dideoxy-D-allopyranose are joined together. The spectra of model compounds and the chlorodeoxycelluloses investigated, obtained by the reaction of cellulose with sulphuryl chloride, are recorded in solution in deuterated dimethyl sulphoxide (DMSO-d_6). The agreement of the chemical shifts of the most intense signals both in the region of the anomeric carbon atoms and in the region of the C(2)—C(6) atoms with the signals of the carbon atoms of the corresponding model compounds showed that 6-chloro-6-deoxy-D-glucose units linked to one another predominate in chlorodeoxycellulose with D.S. = 0.7 and that unsubstituted D-glucose units and a certain number of 3,6-dichloro-3,6-dideoxy-D-allose residues are present. The 3,6-dichloro-3,6-dideoxy-D-allose residues linked to one another predominate in chlorodeoxycellulose with D.S. = 1.5 and there is a small amount of 6-chloro-6-deoxy-D-glucose and unsubstituted D-glucose units. Thus the method makes it possible to establish not only the monosaccharide composition of chlorodeoxycellulose but also the main sequence in which the sugar units forming part of the composition of the polysaccharide are linked together.[12,50]

Some information about the structure of chlorodeoxycellulose can be obtained by the periodate oxidation method.[12] Chlorodeoxycellulose with D.S. = 0.7, obtained by the reaction with sulphuryl chloride, absorbed ~1 mole of the oxidant per mole of the glucopyranose unit of cellulose, which indicates the retention of all the glycol groups of cellulose at the given stage of substitution. Chlorodeoxycellulose with D.S. = 1.5 absorbs 0.5 mole of IO_4 per monosaccharide residue, which means that, when cellulose is treated with sulphuryl chloride, initially the primary hydroxy-groups and then one of the secondary hydroxy-groups are substituted by chlorine atoms.

The method for the determination of unsubstituted primary hydroxy-groups, based on the successive application of reactions involving the tosylation of the hydroxyl-groups and the subsequent substitution of the primary tosyl groups by iodine on treatment with NaI, has been used[41] to determine the position of the halogen in the monosaccharide residues of halogenodeoxycelluloses obtained by the action of Br_2 or Cl_2 in the presence of phosphorus. The number of free primary hydroxy-groups in the halogenodeoxycellulose investigated and hence the amount of halogen attached to the primary carbon atoms are inferred from the amount of iodine introduced. However, such proof of the position of the halogen is not rigorous, since under the conditions governing the substitution of the tosyl group by iodine there is a possibility that the bromine atoms at a primary carbon atom are also substituted by iodine.

A number of workers have used hydrolysis and the study of the composition of the hydrolysate by chromatographic methods (paper and TLC, GLC, and chromatomass-spectrometry) for the determination of the structure of chlorodeoxycelluloses.[13,22,28] However, the incomplete hydrolysis of chlorodeoxycellulose[12,22,28,51] and also the occurrence of side reactions of the sugars with increase of the time during which chlorodeoxycellulose is kept in 72% sulphuric acid from 2 h in the standard method to 16 h [13] or 36 h [28] preclude the derivation of complete information.

IV. THE PROPERTIES OF HALOGENODEOXY-DERIVATIVES OF CELLULOSE

The data accumulated at the present time on various properties of halogenodeoxycelluloses, including those of practical importance such as the resistance to acid hydrolysis, combustion, and enzyme hydrolysis, are widely scattered. Only some workers[22] have published data obtained in a comparative study of the chemical properties as a function of the degree of substitution of halogenodeoxycellulose or the type of halogen introduced.

1. Physical, Physicochemical, and Mechanical Properties

There have been no systematic studies on the physical, physicochemical, and mechanical properties of halogenodeoxycelluloses.

Chlorodeoxycellulose obtained by reaction with $SOCl_2$ in pyridine from mercerised cotton linters is coloured;[21] according to Boechm,[22] the colour deepens with increase of reaction temperature. The replacement of pyridine by the more polar DMF as the solvent leads to the formation of less coloured products.[23] Colourless products are obtained in chloroform and carbon tetrachloride. Chlorodeoxycellulose obtained using methanesulphonyl chloride from soluble sulphide cellulose is slightly coloured after chlorination for more than 2 h.[28] According to Boechm,[22] chlorodeoxycellulose with D.S. = 0.29, 0.67, and 1.04 gives rise to low-viscosity solutions in copper–ammonia solution and only a small proportion of such cellulose can be precipitated from the solution. It has been reported[28] that chlorodeoxycellulose containing 16% of chlorine is soluble in water, while that containing 20% of chlorine is insoluble. Data on the molecular weight distribution of these two chlorodeoxycellulose specimens indicate the absence of the degradation of the polymer during chlorination with methanesulphonyl chloride up to a chlorine content of 16%; when a chlorine content of 20% is attained, the degree of degradation is slight. The molecular weight distribution has been established by gel chromatography using chlorodeoxycellulose nitrate. On chlorination with thionyl chloride, the loss of the fibrous structure of cellulose has been noted.[21] The tensile strength does not decrease on chlorination of methanesulphonylcellulose by alkali metal halides.[32]

2. Chemical Properties

The substitution of some of the hydroxy-groups of cellulose by chlorine hinders the acid hydrolysis of the glycoside linkages between the monosaccharide units in chlorodeoxycellulose.[12,22,28,51] According to Boechm's data,[22] an increase of the D.S. with respect to chlorine from 0.33 to 1.04 entails an increase of the fraction of unhydrolysable residue from 0 to 8.3% under the conditions of the standard two-stage hydrolysis of cellulose; incomplete hydrolysis products are present in the soluble part. 3,6-Dichloro-3,6-dideoxy-derivatives of cellulose with D.S. = 1.6 are almost stable under the conditions corresponding to the hydrolysis of cellulose: under standard hydrolsyis conditions, only 13–20% of the total sugars pass into solution (via the reaction with the phenol–H_2SO_4 reagent).[12] Chlorodeoxycellulose with D.S. = 2.8 is fully resistant to acid hydrolysis.[51] There are data indicating the resistance of the C–Cl bond in chlorodeoxycellulose to acid hydrolysis: when $AgNO_3$ is added to the chlorodeoxycellulose hydrolysate, only traces of AgCl are formed.[22]

The elimination of the halogen from chloro- and bromodeoxycelluloses on treatment with 1 *N* NaOH solution has been investigated as a function of temperature (20–100 °C) and reaction time (30–120 min).[41]

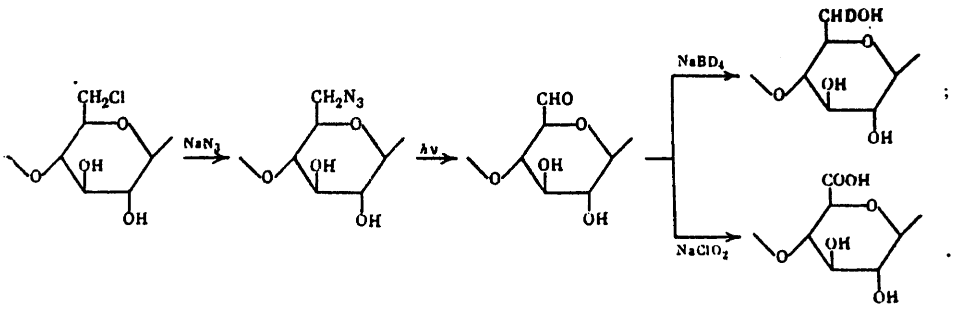
According to the data of a number of workers, the introduction of a halogen into cellulose increases its resistance to combustion. In terms of their resistance to inflammation, methanesulphonyliodo- and methanesulphonylbromo-deoxycelluloses are superior to the initial methanesulphonylcellulose and methanesulphonylchlorodeoxycellulose.[32] Judging from the length of the charred region, the area of charring, and the residence time of the ash in the hot state, chlorodeoxycellulose is much more resistant to burning than cellophane and is little inferior in this respect to poly(vinyl chloride).[8]

According to thermogravimetric data, chlorodeoxycellulose produces more water and carbon and less tar on decomposition than does cellulose.[52] The difference in the behaviour of cellulose and chlorodeoxycellulose has been explained by reactions involving the elimination of HCl from chlorodeoxycellulose. Chlorodeoxycellulose has been investigated by special methods and also by IR spectroscopy, X-ray diffraction, and thermogravimetric measurements. It has been established that the Cl atom bound chemically in chlorodeoxycellulose or added to cellulose in the form of chlorine-containing paraffins has little influence on the combustibility of the materials.[53] The combination of Cl atoms and added Sb_2O_3 effectively retards combustion (the introduction of Sb_2O_3 alone is ineffective). It has been suggested that the synergism in the action of the above agents is associated with the catalytic acceleration of the dehydration of chlorodeoxycellulose, which is accompanied by the formation of a thermostable polyene structure.[53]

The study of the morphology of the charring of chlorodeoxycellulose fibres by scanning electron microscopy has shown that their thickness appreciably diminishes under these conditions, in contrast to the fibres of cotton treated with fireproofing agents.[54]

Chlorodeoxycellulose obtained by the reaction with thionyl chloride, methanesulphonyl chloride, or phosphoryl chloride has been frequently used as the starting compound for the preparation of new deoxy-derivatives of cellulose by the nucleophilic substitution reactions with KSCN,[33] NH_3, NH_2NH_2, KCN,[23,55,56] $HSCH_2COOH$, RNH_2,[24] diethylenetriamine,[57] ethylenediamine, thiourea, thiosemicarbazide, thioacetamide,[58] and 1,6-diaminohexane.[59] Cellulose phosphonimidate has been synthesised by the reactions of chloro- and bromodeoxycelluloses with phosphoramidites.[60] Mercaptodeoxycellulose has been obtained from chlorodeoxycellulose.[61,62]

The nucleophilic substitution reaction between chlorodeoxycellulose and sodium azide has been studied in greatest detail.[13] Chlorodeoxycellulose with different D.S. (0.12, 0.37, and 0.67) was treated with sodium azide in DMF, water, and DMSO:



It was established that, when the reaction is carried out in DMF, the degree of polymerisation falls from 506 to 153, whereas in water the fall is to 448 and in DMSO to 463. Furthermore, in the presence of DMSO the greatest degree of conversion of the halogenodeoxy-groups into azidodeoxy-groups was noted. Further reactions of azidodeoxycellulose take place quantitatively and serve as proof of the structures of both azido deoxycellulose and the initial chlorodeoxycellulose.

Another reaction of halogenodeoxycelluloses which has been studied in detail is their reduction. The reduction of 6-halogeno-6-deoxycellulose by various reducing agents in order to obtain 6-deoxycellulose has been investigated by a number of workers.[9,10,20,63]

When 6-iodo-6-deoxy-2,3-di-*O*-tosylcellulose is reduced with zinc in methanol, the iodine content falls only from 28 to 22%, while on reduction with sodium in dioxan it diminishes from 34 to 6%.[63] The formation of C=C bonds in the reaction product was noted in the latter case, which indicates the simultaneous occurrence of the HI elimination reaction.

The reductive elimination of phenylcarbamate groups from 6-chloro-6-deoxy-2,3-di-*O*-phenylcarbamoylcellulose on treatment with $LiAlH_4$ in THF is accompanied by the elimination of chlorine: 25% of chlorine is eliminated after 1 h and the chlorine is lost entirely after 5 h. 6-Deoxyglucose and glucose were detected by paper chromatography in the reaction product after its hydrolysis.[20]

The reaction conditions and the structure of the products were investigated most completely in the reduction of 6-chloro-, 6-bromo-, and 6-iodo-6-deoxycelluloses with $NaBH_4$ in DMSO.[9,10] 6-Deoxycellulose with the highest content of 6-deoxyglucopyranose units (~80%) compared with the products obtained previously in other reactions was produced by the reduction of 6-bromo-6-deoxycellulose. The bromodeoxy- and iododeoxyglucopyranose units are then quantitatively converted into 6-deoxyglucopyranose units; apart from the 6-deoxyglucopyranose residues, the final product contains only the unchanged glucopyranose units.

Halogenodeoxycellulose has been frequently used to obtain 5,6-cellulosene by the reaction involving the elimination of a hydrogen halide molecule with alkali. When 6-iodo-6-deoxycellulose is treated with 9–10% alcoholic alkali for 1–2 days at 20–70 °C, a mixed cellulose derivative containing 5,6-glucosene, 3,6-anhydroglucopyranose, and glucopyranose residues is formed.[37,64,65] The use of potassium t-butoxide in DMSO makes it possible to achieve the quantitative conversion of chlorodeoxycellulose into 5,6-cellulosene.[27]

The photoinitiated grafting of methyl methacrylate on chlorodeoxycellulose has been achieved.[66]

3. Biochemical Properties

The enzyme hydrolysis of 6-chloro-, 6-bromo-, and 6-iodo-6-deoxycelluloses by the cellulases from *T.viride* and *A.niger* has been investigated and compared with that of 6-deoxycellulose and cellulose hydrate which are the starting materials in their synthesis.[67] From the accumulation of non-reducing and reducing sugars in the hydrolysates, it was established that, under conditions optimal for the enzyme hydrolysis of cellulose hydrate, the specimens of the modified celluloses are also cleaved by the *T.viride* cellulase. However, the hydrolysis is not complete. The obstacles to enzyme hydrolysis increase with increasing bulk of the substituent: H < Cl < Br < I. The reactions involving the formation of non-reducing sugars are hindered to a greater extent than the reactions resulting in the formation of reducing sugars. Among the soluble products of the enzyme hydrolysis of 6-chloro-, 6-bromo-, and 6-iodo-6-deoxycelluloses, there is no modified monosaccharide. The joint action of the *T.viride* and *A.niger* cellulases leads to the formation (according to paper chromatographic data) of a certain amount of modified monosaccharide from 6-chloro-6-deoxycellulose with D.S. = 0.3 and 0.9.

V. PRACTICAL APPLICATIONS

Although halogenodeoxycelluloses have properties important from the practical point of view such as resistance to inflammation and acid and enzyme hydrolysis, they have not themselves found applications as yet. It is noteworthy that their resistnace to acid and enzyme hydrolysis has been discovered comparatively recently, the possibility of using for their synthesis sulphuryl chloride—the most readily available, cheapest, and most effective halogenating agent. However, there exist many recommendations for the employment of halogenodeoxycelluloses in the synthesis of deoxy-derivatives of cellulose of practical importance.

In order to render cotton fabric creaseless, the latter is treated with phosphoryl chloride in DMF at 65–78 °C for 0.5–1 h.[68] The chlorodeoxycellulose formed is treated with a 1–10% solution of ethylenediamine hydrogen sulphite in ethylenediamine. The resulting cellulose, cross-linked by polysulphide linkages, has effective creaseless properties: the opening angle is 210–300°, while more than 65% of the strength is retained. However, owing to the appearance of a yellow colour in the fabric, this method has not found a practical application.

In order to obtain a cationic polyelectrolyte capable of adsorbing transition metal ions, particularly mercury and copper ions, microcrystalline cellulose is activated with a 20% NaOH solution and is treated with thionyl or methanesulphonyl chloride in DMF at 90–100 °C for 1.5–16 h.[69] The resulting deoxycellulose is acted upon by hydrazine hydrate at 70–110 °C for 1–60 h. It has been suggested that the resulting hydrazinodeoxycellulose be used for analytical (detection of traces of polyvalent metals) and technological (purification of sewage) purposes.[69]

Compounds useful as adsorbents have been obtained by the reaction of chlorodeoxycellulose with diethylenetriamine,[57] ethylenediamine, thiourea, thiosemicarbazide,[58] 1,6-diaminohexane,[59] and other compounds. 2,2'-Diaminodiethylaminodeoxycellulose, obtained by the method of Smits and van Grieken,[57] is characterised by an ion-exchange capacity of 2.4 μequiv.cm^{-2} in relation to variable-valence metals. The limiting concentrations of iron, zinc, and copper ions detectable in one litre of water with the aid of membranes prepared from the given derivative are 1.5×10^{-7}, 0.5×10^{-7}, and 0.2×10^{-7}% respectively. The cellulose derivatives obtained by the method of Tashiro and Shimura[58] remove mercury ions from aqueous $HgCl_2$ solutions (concentration 1×10^{-3}%) to an extent greater than 99%. The mercaptodeoxycellulose obtained from chlorodeoxycellulose is used to immobilise enzymes and also as carriers for chromatography.[62,70]

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Analysis of the available data shows that the chemistry of halogenodeoxycelluloses has developed significantly in recent years.

A series of halogenating agents, new as regards cellulose, have found applications in the synthesis of halogenodeoxycelluloses. The possibility of using a readily available, cheap, and effective halogenating agent, namely sulphuryl chloride, for the synthesis of chlorodeoxycellulose with different D.S. has been demonstrated. A method has been developed for the introduction of any halogen (Cl, Br, or I) in the C(6)-position in the glucopyranose unit of cellulose under comparable conditions. Fluorodeoxycellulose with a high D.S. has been synthesised. Approaches have been outlined towards the selective substitution of the secondary hydroxy-groups in cellulose by halogen. The behaviour of a series of blocking functional groups in the reactions involving the substitution of the hydroxy-groups by a halogen and methods for their successive elimination in the presence of a halogen have been investigated.

New methods for the determination of the position of the halogen in the glucopyranose unit of halogenodeoxycellulose have appeared. A quantitative chemical procedure for the determination of the structures of 6-bromo- and 6-iodo-6-deoxycelluloses has been developed. A method has been devised for the establishment of the structure of chlorodeoxycellulose by ^{13}C NMR. Apart from the position of the halogen atom, the latter makes it possible to determine the stereochemistry of the process involving the substitution of the secondary hydroxy-groups by chlorine and the sequence in which the sugar residues, differing in the number, positions, and stereochemistry of halogen atoms, are linked to one another.

The physicochemical and other properties of halogenodeoxycelluloses have been little studied. The investigation of the biochemical properties, in particular the enzyme hydrolysis reactions, has only just begun.

A series of derivatives, which are difficult or are altogether impossible to obtain by other methods, have been synthesised from chlorodeoxycellulose. Some of them have found novel applications (for the immobilisation of enzymes and as adsorbents).

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The Physical Chemistry of Energy-saturated Media

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The physicochemical properties of ultradispersed media, as a particular case of energy-saturated media, have been reviewed. The size dependence of the temperatures of fusion, polymorphic transformation, and sintering, the diffusion coefficients, and the chemical activity of ultra-small particles have been explained from a single viewpoint. Methods for obtaining ultradispersed powders, and methods for producing an ultradispersed structure in metals and alloys, have been described.
The bibliography contains 96 references.

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I. INTRODUCTION

Energy-saturated media are media into which an excess of energy, comparable with the internal energy of the equilibrium condensed medium, has been introduced by some means. An energy-saturated medium can be produced by dispersal of the substance, plastic deformation of solids, quenching of a metastable structure or a supersaturated solution in alloys, irradiation of solids with a beam of neutrons or hard γ-radiation, etc.

In practice, a combination of these methods is most frequently used. Irrespective of the method used to obtain the dispersed system, its excess energy is determined either by the surface energy or by the formation of metastable solutions (in particular by an increase in the limiting solubility of inert gases in small particles). At the lower limit of the particle size of dispersed systems (<5 nm), that is in ultradispersed (UD) media, the contribution of these forms of energy is comparable with the internal energy, so that the definition of energy-saturated media is satisfied, in particular, by UD media.

Cooling a melt sufficiently rapidly (up to 10^6 K s^{-1}) makes it possible to fix metastable structures (phases), supersaturated solid solutions, and systems with dispersed phase components.

The deformation of metals and alloys leads to the appearance of dislocations, disclinations, and vacancies, and hence to saturation by an excess of energy if the relaxation time is sufficiently long.

The irradiation of a solid by neutrons, a beam of charged particles, or hard electromagnetic radiation produces radiation defects: vacancies and interstitial atoms, accumulations of vacancies, and impurity atoms (on neutral irradiation or as a result of ion implantation), again leading to energy saturation.

All states of this kind are non-equilibrium states. In some cases they are metastable states (when the system is at an intermediate energy minimum), and in other cases they are kinetically hindered states. The present review deals only with states for which the relaxation time is sufficiently long for local equilibrium to be established, and in a number of cases a thermodynamic approach can be used to discuss these systems. The chief characteristics of these media will be discussed for the case of UD media.

Ultradispersed media (UDM) represent unique states of condensed substances—macroscopic ensembles of ultra-small particles with dimensions reaching about 10 nm. The unusual properties of UD systems may be due both to the characteristic features of the individual ultra-small particles present in the ensemble and to their collective behaviour, determined by the nature of the interaction between them. In UDM, the surface states acquire particular importance, since in an ultra-small particle the number of atoms on the surface becomes comparable with the number of atoms in the bulk, so that the contribution of the surface energy to the total energy of the particle becomes comparable with that of the bulk energy. Thus for the liquid droplets of aluminium at 10^3 K, the proportion of excess (surface) energy relative to the bulk energy increases from 9% to 45% with decrease in the particle size from 10 nm to 20 nm.[1] The developed surface influences the lattice and electronic subsystems of the UDM, changing the spectra of various elementary excitations sensitive to change in the symmetry and the boundary conditions. The interaction of the particles in the system determines those physical properties of the UDM resulting from the correlation of the electronic and phonon states of the system. Finally, the presence of a large excess of energy in the ultra-small particles leads to an increase in their chemical activity, and this on the one hand must be taken into account in their preparation (the problem of "passivation") but on the other hand can be used in various technological processes.

A basis for the physical chemistry of UDM is provided by the theory of heterophase fluctuations,[2] the physicochemical mechanics of materials,[3] the thermodynamics of "small" systems,[4,5] and the fundamental postulates of thermodynamics and statistical physics.[6]

In the last 10 years, the properties of ultradispersed metal particles and powders (UDP) have been actively studied,[7–9] the properties of clusters in ultra-fine channels, in particular in the pores of zeolites, have been studied,[10] plasma-chemical methods for obtaining UDP[11–14] and methods for the thermal decomposition of solid substances[15] have been developed, new properties of ultradispersed carbon materials have been studied,[16,17] the thermodynamics of metastable states and methods for producing ultradispersed structures in compact solids under synthesis conditions and with plastic deformation,[17–21] and the technology of the production of heat-resistant amorphous alloys,[22] have been developed, and the physicochemical properties of materials with ultradispersed structures have been studied.[23]

An important methodological addition to the physicochemical analysis of metastable (ultradispersed) systems is the need to take account of not only the composition and physicochemical and mechanical properties but also the structural characteristics of the reaction products. An important structural characteristic of a material is its degree of dispersion. The three-term formula of classical physicochemical analysis, "composition–structure–property", can be supplemented by the additional term "degree of dispersion". This is particularly obvious for materials with degrees of dispersion at the lower limit of the size of the structural fragments. Thus in compact form the extended equation of physicochemical analysis[24] has the following form:

Composition	Structure	Degree of dispersion	Property
Atomic, molecular (mass) from 0 to 100%	Determined by X-ray diffraction or spectroscopy (infrared, NMR, Mössbauer, EPR, etc.), and also determination of structural defects (dislocations, defects, associations of defects)	From monoatomic or molecular to single crystals, including the colloidal state	All measurable properties (physics, thermodynamics, mechanics, resistance of materials)

The introduction of the degree of dispersion into the basic equation of physicochemical analysis requires firstly the accumulation of the appropriate experimental data. This is done using the methods of modern experimental physics: X-ray, electron, and neutron diffraction, Auger, photoelectron, and infrared spectroscopy, secondary ion mass spectrometry, nuclear and electronic magnetic resonance, and the methods of crystal chemistry.

The effects of size on physicochemical properties, clearly revealed in ultradispersed systems, are used in various practical technological processes. For example, the production of a system of ultrafine channels from powders makes it possible to use capillary effects in low-temperature soldering processes. Ultradispersed powders can provide a basis for the production of pastes for the permanent joining of materials of different kinds, and also for the development of composition materials with improved physicomechanical properties for the production of tungsten-free hard alloys and special optical and other materials. The use of UDM as additives in powder metallurgy (for example in sintering) decreases considerably the energy of the activation processes. Promising possibilities are provided by the electrophysical properties of powdered pure metals and their compounds (nitrides, carbides, borides, etc.), which can be used as superconducting and semiconducting materials and as getters, catalysts, and filters with improved properties. The products of a stable ultradispersed structure in compact materials leads to an increase in their strength up to the theoretical value and to increased values of the hardness and toughness.

The use of energy-saturated and in particular ultradispersed media is now one of the most important conditions for the development of the new technology in various branches of the national economy. The importance of this field is the reason for the development of intensive studies in the USSR and other countries (West Germany, Japan, the USA, France, Sweden, etc.).

The solution of the problems associated with the technological application of energy-saturated media, leading to direct "production of materials", is not a remote possibility. The comprehensive development of this field of study is therefore now necessary.

II. THE PHYSICOCHEMICAL PROPERTIES OF ENERGY-SATURATED MEDIA

1. The Thermodynamics of Small Systems. The Minimum Size of Particles with the Characteristics of the Phase

The thermodynamic and statistical-mechanical approaches to the study of the theory of UDM have developed fruitfully in recent years. In the thermodynamic approach, difficulties arise, associated with the limiting change to small systems. Classical thermodynamics and statistical physics no longer "operate" with decrease in the particle size to 1 nm.

When the degree of dispersion is introduced into the thermodynamic description, the energy of the system is no longer a linear homogeneous function of its variables;[5] an additional degree of freedom appears, namely the size of the particles in the ensemble, or in other words the degree of dispersion. According to the criteria adopted, this requires additional coordinates in the equilibrium diagrams. The physicochemical analysis of inorganic materials is therefore complicated considerably, particularly in the case of multi-component systems.

The non-additivity of the thermodynamic functions, due to the contribution of the phase interface, is taken into account in Gibbs thermodynamics by introducing the surface tension σ, related in definite fashion to the chosen interface surface, and leads to size effects of first order for the principal thermodynamic quantities. The extension of the thermodynamic approach to the range of small particle sizes (r < 5–7 nm), which is justified in the examination of ensembles of these particles, makes it necessary to take account of the size dependence $\sigma(r)$, and hence leads to second-order size effects for the principal thermodynamic quantities characterising the small system. It will be shown that σ decreases with decrease in r, leading to the lowered values of the Laplace pressure p_L, that is to a decrease in the proportion of the surface energy, which is characterised by p_L, relative to the bulk energy, compared with the result of the calculation for $\sigma = \text{const}$. Thus the first-order size effects are due to the basic non-additivity of the thermodynamic functions, whereas the second-order effects based on them are due to the elimination of this non-additivity and the approach of the bulk and surface states in a small particle. The second-order size effects represent the most characteristic feature of the physical chemistry of UDM. Their introduction makes it possible to extend considerably the range of applicability of the thermodynamic description to particles with small dimensions.

Using the thermodynamic approach, Tolman[25] obtained the following expression for $\sigma(r)$:

$$\ln\frac{\sigma(r)}{\sigma_s}=\int\limits_{\infty}^{r}\left\{\frac{2\sigma}{r^2}\left[1+\frac{\delta}{r}+\frac{1}{3}\left(\frac{\delta}{r}\right)^2\right]\right\}dr\Big/\left\{1+\frac{2\delta}{r}\left[1+\frac{\delta}{r}+\frac{1}{3}\left(\frac{\delta}{r}\right)^2\right]\right\} \tag{1}$$

where σ_s is the surface tension of the planar phase interface, and $\delta = r_e - r$ the difference between the radii of the equimolar surface and the tension surface. In the general case the $\delta(r)$ relationship is not known. The determination of the $\delta(r)$ relation requires the statistical-mechanical calculation of the profiles of the density and the pressures of the inter-phase region for a real spherical structure corresponding to the given supersaturation. These calculations are fairly complex, and require the selection of some "single equation of state", by means of which, given the supersaturation of the vapour, it is possible to calculate the parameters of the pressure of the macroscopic condensed phase in equilibrium with it at a given temperature, to determine the density profile of the spherical formation, and to find the position of the equimolar surface and, from the profile of the basic pressures, the position of the tension surface. In addition, in the statistical-mechanical calculation it is necessary to make various assumptions associated with the description of the inter-phase region.

The following method for the closure of Tolman's expression (1) has been proposed.[26] The difference between the equimolar volume $V_e = 4\pi r_e^3/3$ and the tension volume $V = 4\pi r^3/3$ is related to the dispersion of the equimolar volume:

$$(\overline{(\Delta V_e)^2})^{1/2}=(kT\varkappa_T V_e)^{1/2},\ \text{that is}\quad V_e-V=a\,(kT\varkappa_T V_e)^{1/2} \tag{2}$$

where a is a correction factor, and κ_T the isothermal compressibility. Expressing r_e from Eqn.(2) in terms of r gives a $\delta(r)$ relationship of the form:

$$\delta(r)=\frac{r_0}{6^{1/3}}\left\{1+\left[1+6\left(\frac{r}{r_0}\right)^3\right]^{1/2}\right\}^{2/3}-r,\quad r_0=\left(\frac{9kT\varkappa_T a^2}{8\pi}\right)^{1/3} \tag{3}$$

Integrating Eqn.(1) with allowance for Eqn.(3) gives the explicit form of the expression for $\sigma(r)$:

$$\frac{\sigma(r)}{\sigma_s}=\left(\sqrt{1+y}+\frac{\sqrt{y}}{3}\right)^{1/3}(\sqrt{1+y}-\sqrt{y});\quad y=\frac{1}{6}\left(\frac{r_0}{r}\right)^3 \tag{4}$$

In the range of small dimensions ($r \ll r_0$), Eqn.(4) gives a physically justified linear relationship $(\sigma(r)/\sigma_S) = r/r_0 + \ldots$, and the slope of the straight line is determined by the characteristic dimension r_0. At high $r \gg r_0$, the approach of σ to σ_S is described by the approximation

$$\frac{\sigma(r)}{\sigma_s}=1-\frac{2}{3}\left(\frac{2}{3}\frac{r_0}{r}\right)^{3/2}+\ldots$$

that is the influence of slight curvature on the surface tension is proportional to $r^{-3/2}$, in complete agreement with the results of statistical-mechanical calculations.[27]

Since Eqn.(2) contains the unknown factor a, the parameter r_0 can be found only by comparing the experimental $\sigma(r)$ relationship. These experimental data are not available, however. Another possibility is to consider data on the spinodals of the substance. This procedure[28] is based on the assumption that at the boundary of stability of the homogeneous original phase, that is on the spinodal defined by the condition $(\partial p_0/\partial v_0)_T = 0$, both the radius r of the tension surface of the critical nucleus of the new phase and the tension corresponding to this surface σ become zero. Here, ν_0 is the volume corresponding to one mole of the vapour.

The radius of the tension surface of the critical nucleus of the competing phase satisfies the equations

$$\begin{cases} p_1-p_0=\dfrac{2\sigma}{r} & (5)\\ \mu(p_1,T)=\mu_0(p_0,T) & (6)\end{cases}$$

where 1 and 0 are the indices of the parameters of the liquid and vapour respectively. On going deeper into the metastable range as $p_0 \to p_2$ (the pressure on the spinodal), the size of the critical nucleus $r \to 0$, but the decrease in $\sigma(r) \sim r$ leads to the final value of the left-hand side of Eqn.(5). The approximation of Eqn.(4) in the range of small dimensions gives the expression

$$(p_1-p_0)\big|_{p_0\to p_2}=\frac{2\sigma}{r}\bigg|_{r\to 0}=\frac{2\sigma_s}{r_0} \tag{7}$$

When $p_2(T)$ is known, the difference between the pressures in the left-hand side of Eqn.(7) can be determined from Eqn.(6). For two infinitely close states of equilibrium of the critical nucleus with the metastable vapour it is possible to write

$$d\mu_1(p_1,\ T)=d\mu_0(p_0,\ T)$$

or at constant temperature

$$\int\limits_{p_s}^{p}v_1dp_1=\int\limits_{p_s}^{p_0}v_0dp_0 \tag{8}$$

The index s relates to quantities on the binodal. Neglecting the compressibility of the liquid ($\nu_1 = \nu_{1S} = \text{const}$) and regarding the vapour as an ideal gas ($\nu_0 p_0 = p_S \nu_{0S}$), Eqn.(8) with allowance for Eqn.(5) yields:

$$\frac{2\sigma}{r}=\frac{p_s v_{0s}}{v_{1s}}\ln\frac{p_0}{p_s}-(p_0-p_s) \tag{9}$$

If in Eqn.(9) the last term is neglected and $p_S v_{0S}$ is replaced by kT, it is possible to obtain the familiar Kelvin equation: $\ln(p_0/p_S) = 2\sigma v_{1S}/kT$. The ideal-gas approximation is fairly crude in the metastable range, but the proposed[29] relation of the isotherm of an ideal gas not to the far range of the true isotherm, where they are in fact similar, but to the condensation point, reduces the error of the approximation considerably.

Equating p_0 in Eqn.(9) to p_2, and allowing for Eqn.(7), gives for the parameter $r_0(T)$ an expression of the form:

$$r_0 = 2\sigma_s \Big/ \left[\frac{p_s v_{0s}}{v_{1s}} \ln \frac{p_2}{p_s} - (p_2 - p_s) \right] \tag{10}$$

If in Eqn.(3) $r = 0$, then $\delta_0 = (2/3)^{1/3} r_0$.

Thus the fluctuation approach, supplemented by the spinodal procedure, makes possible not only the closed calculation of the $\sigma(r)$ relationship but also the estimation of the minimum spinodal diameter of the competing phase $2\delta_0$.

The problem of finding the minimum size of the nucleating phase is related to the fundamental problem of determining the size limit of applicability of the thermodynamic description of small systems. A rigorous definition of thermodynamic concepts is possible only in the limit $N, v \to \infty$, $N/v \to$ const, that is for a large system. The use of the thermodynamic concepts of small systems is justified only in the examination of not an individual small particle but an ensemble consisting of n identical particles. As $n \to \infty$, the ensemble becomes a macroscopic system, no matter how small its component subsystems, and the use of the thermodynamic approach becomes fully justified. The minimum size of the new formation and the deviation from homogeneity which would make it possible to speak of the appearance of a new phase can be considered. As already shown, the systematic extension of the Gibbs—Tolman ideas to the range of small dimensions leads to the boundary condition $\sigma = 0$ with the disappearance of the tension surface ($r = 0$). The radius of the equimolar surface is non-zero and equal to δ_0. Since this radius characterises most accurately the size of the physical inhomogeneity, it is natural to regard it as the minimum size, beyond which the separation of the system into different phases loses meaning. The condition of disappearance of the tension surface corresponds to the disappearance of the nucleus of the new formation, that is the entire small "particle" is an interphase particle, so that it is now not a particle of a new phase, but a cluster. The same condition can alternatively be called the spinodal limit of stability of the homogeneous phase with respect to the appearance in it of the nucleus of a competing phase, since the work of nucleus formation also becomes zero. A clear boundary is thus drawn between homogeneous and heterogeneous states.

2. Change in the Phonon Spectrum with Decrease in the Particle Size

It is natural to try to describe the properties of an ultra-small particle by the methods of statistical physics. If the atoms in a cluster can undergo vibrations about equilibrium positions, and the cluster as a whole can undergo rotations and translations, then the partition function can be represented as the product of the translational Z_{tr}, rotational Z_{rot}, and vibrational Z_{vib} partial partition functions:

$$Z(N, T) = Z_N^{rot}(T) Z_N^{tr}(T) Z_{vib}(N, T) e^{-U_0(N)/kT} \tag{11}$$

Here, $U_0(N)$ is the minimum value of the potential energy of the cluster. To calculate $Z_N^{tr}(T)$ it is necessary only to know the mass of the cluster; $Z_N^{rot}(T)$—the moment of inertia of the cluster (that is it is necessary to have an idea of the shape of the cluster); and $Z_{vib}(N, T)$—the frequencies ν_i of the normal vibrations of the system, which can be found from the expression for the potential energy of the system:

$$U(N) = \sum_i^N \sum_{j \neq i}^N U(r_{ij}) \tag{12}$$

where $U(r_{ij})$ is the potential of the interaction between the atoms, of the Lennard—Jones or Morse type.

By expanding $U(N)$ in a series with respect to powers of the Cartesian coordinates of small displacements of the atoms from their equilibrium positions and restricting to harmonic terms, it is possible to calculate the magnitude of the forces acting on the atoms and to write the equations of motion of the atoms. Changing from Cartesian to normal coordinates gives a system of $3N - 6$ independent equations, whose determinant gives the frequencies of the $3N - 6$ modes. A knowledge of the spectrum of the normal vibrations (the phonon spectrum) makes it possible to calculate $Z_{vib}(N, T)$, and hence the thermodynamic characteristics of the cluster.[30]

Direct mechanical methods (of molecular dynamics) of calculating the properties of the clusters are also used. In this case, for each atom, a system of ordinary equations of motion under the influence of the forces is written,

$$\overline{F}_i = -\sum_{j=1}^{N-1} \nabla U(r_{ij}),$$

where $U(r_{ij})$ is also the pair interaction potential. The magnitude of the calculation increases in avalanche fashion with increase in the number of particles, so that the possibilities of the method are determined by the possibilities of the computers used.[31] The machine methods also include the Monte Carlo method.[32]

The phonon spectrum of small particles show low-frequency modes which are not present in the spectrum of large crystals.[33–35] These "soft" modes are related to the surface vibrations, and change irregularly with change in the size of the cluster: the spectrum depends on the geometry of the equilibrium configuration. The thermodynamic characteristics also change irregularly. The "soft" surface modes lead to increased values of the heat capacity for small particles at low temperatures, as follows from the form of the vibrational part of the partition function

$$Z_{vib}(N, T) = \prod_{i=1}^{3N-6} \exp\left(-\frac{h\nu_i}{2kT}\right) [1 - \exp(-h\nu_i/kT)]^{-1} \tag{13}$$

The change in the low-frequency part of the phonon spectrum is due to the fact that the longest wavelength of elastic vibrations should not be greater than twice the maximum dimension of the crystal and is determined by the shape of the solid, the boundary conditions, and the wave velocities. The density of the frequency spectrum of a small cube with edge dimensions a can be written in the form:[30]

$$g(\nu) = 4\pi a^3 w^{-3} \nu^2 - a^2 w^{-2} \nu - 0{,}125 a w \tag{14}$$

where $w^{-3} = w_l^{-3} + 2w_t^{-3}$ is the average rate (defined in terms of the rates of the longitudinal w_l and transverse w_t vibrations), and the total number of these normal vibrations is

$$3N = \int_{\nu_{min}}^{\nu_{max}} g(\nu)\, d\nu.$$

For a large crystal, the second and third terms in $g(\nu)$ can be neglected, $\nu_{min} = 0$. Thus $\nu_{max}^3 = 9Nw^3/4\pi a^3$, and the Debye frequency $\theta = h\nu_{max}/k$. For a small particle it is necessary to take account of the low-frequency cut-off of the spectrum ($\nu_{\min} \neq 0$), and in this case the use of the familiar relationship

$$E = \int\limits_{\nu_{\min}}^{\nu_{\max}} h\nu g(\nu)\,[\exp(h\nu/kT) - 1]^{-1}\,d\nu \qquad (15)$$

gives the dependence of the heat capacity $C_V = (\partial E/\partial T)_V$ on size in terms of $\nu_{\min}$, and also, with change in the interatomic distances, in terms of $\nu_{\max}$. The Debye temperature θ for a small spherical particle depends on the radius R:[36]

$$\theta \approx \theta_\infty + \theta_\infty(2G\sigma\varkappa - 3w/16\nu_{\max})/R \qquad (16)$$

where $G = -\partial \ln \theta_\infty / \partial \ln \nu$ is the Gruneisen constant, κ the isothermal compressibility, and σ the surface tension. This description of the phenomena is naturally qualitative. For gold particles with $R = 10$ nm, $\theta = 0.966\theta_\infty$, and for $R = 1$ nm, $\theta = 0.92\theta_\infty$. The same trend is observed experimentally.[37]

3. Phase Transformations in Ultra-small Particles

If the size of the cluster exceeds the minimum spinodal diameter, a particle of a new phase is produced. The morphology of relatively large metal particles does not differ from Wolff polyhedra, but for very fine particles the deviations become appreciable. The particles of face-centred cubic metals with dimensions up to 20 nm have dodecahedral and icosahedral forms. A dodecahedral particle can be represented as a combination of five tetrahedra. Twenty tetrahedra with a common vertex give the other stable configuration, that is the icosahedron. The presence in these crystals of five-fold symmetry axes, not characteristic of the massive crystals, indicates that at a definite size of this repeatedly twinned particle, a polymorphic transformation should take place to give the structure characteristic of large particles of the given metal. Repeated twinning of tetrahedra cannot give a continuous "framework", and between some of the twins, gaps filled with an amorphous phase, or stresses distributed through the entire particle, will be produced. The stability of small metal particles with dimensions of 1.5–1.6 nm has been examined theoretically.[33] It was found, for example, that particles of gold, silver, and copper with a diameter smaller than 10.7, 7.6, and 6.8 nm respectively have an icosahedral structure, and that larger particles have the normal face-centred cubic structure. Aerosil particles of most substances with dimensions ≥ 20 nm in fact have the structure of the massive crystal.[30] Thus after the growing particle reaches a certain size, a phase transformation from the icosahedral to the usual structure takes place.

Calculations by the methods of molecular dynamics[38] of the temperature dependence of the total energy show that the temperature–energy diagram contains a section corresponding to heating, a horizontal plateau corresponding to a phase transformation, and a section corresponding to supercooled states of the liquid. This indicates that the concepts of "solid" and "liquid" are also applicable to very small particles. Measurements on UDP show that particles with $R \cong 5$ nm melt at 200–400 K.[37,39,40] This also applies to polymorphic transformations. An example is provided by the transition metals W, Mo, and Nb. The massive specimens have a body-centred lattice (β-phase), but thin films (and small particles) have a face-centred cubic structure (α-phase).[41]

An expression can be written for the chemical potentials of the melt (L) and the α- and β-phases with allowance for the dimensions of fragments of the corresponding phase of n atoms

$$\begin{gathered}
\mu_L = \mu_\beta^0 + \lambda\left(1 + \frac{T}{T^0_{\text{fusion}}}\right) + \frac{2}{3}\alpha_L\sigma_L v_L^{2/3} n^{-1/3} \\
\mu_\beta = \mu_\beta^0 + \frac{2}{3}\alpha_\beta\sigma_\beta v_\beta^{2/3} n^{-1/3} \\
\mu_\alpha = \mu_\beta^0 - \lambda_{\alpha\beta}\left(1 - \frac{T}{T^0_{\alpha\beta}}\right) + \frac{2}{3}\alpha_\alpha\sigma_\alpha v_\alpha^{2/3} n^{-1/3}
\end{gathered} \qquad (17)$$

Here, α_i ($i = L$, α, β) are the form coefficients, σ_i the surface energy, and ν_i the volume per atom in the melt and in the α- and β-phases respectively; λ and T^0_{fusion} the heat and temperature of fusion; and $\lambda_{\alpha\beta}$ and $T^0_{\alpha\beta}$ the heat and temperature of the α–β transformation of the massive specimen. Since μ_L and μ_β are equal on the equilibrium line, an expression is obtained for the dependence of the melting point of the particle on the size n, the shape α_β, and the density ρ_β:

$$\frac{T^0_{\text{fusion}} - T_n}{T^0_{\text{fusion}}} = \frac{2m_0^{2/3}}{3\lambda}\left(\frac{\alpha_\beta\sigma_\beta}{\rho_\beta^{2/3}} - \frac{\alpha_L\sigma_L}{\rho_L^{2/3}}\right) n^{-1/3} \qquad (18)$$

Here, m_0 is the mass of the atom, and T the melting point of a particle containing n atoms. Since $\rho_\beta \cong \rho_L$, $\sigma_\beta > \sigma_L$, and, usually, $\alpha_\beta > \alpha_L$ (faceting takes place), then $T_n < T^0_{\text{fusion}}$, that is the melting point of the ultra-small particles is lowered.

Similarly, since μ_β and μ_α are equal on the equilibrium line,

$$\frac{T^0_{\alpha\beta} - T_{\alpha\beta}}{T^0_{\alpha\beta}} = \frac{2m_0^{2/3}}{3\lambda_{\alpha\beta}}\left(\frac{\alpha_\alpha\sigma_\alpha}{\rho_\alpha^{2/3}} - \frac{\alpha_\beta\sigma_\beta}{\rho_\beta^{2/3}}\right) n^{-1/3} \qquad (19)$$

Since $\alpha_\alpha \cong \alpha_\beta$, $\sigma_\alpha \cong \sigma_\beta$, and $\rho_\beta < \rho_\alpha$, the difference in brackets is negative, and the temperature of the polymorphic transformation of the ultra-small particle $T_{\alpha\beta}$ is higher than $T^0_{\alpha\beta}$ for the massive specimen. From this it is clear that in a certain range of temperatures, as the film becomes thinner, the β-phase may be converted into the α-phase, metastable with respect to the massive equilibrium specimen, as observed in experiments with films of W, Mo, and Nb.[41]

As far as the mechanism of the fusion of the particles is concerned, Petrov,[30] for example, considers that the most acceptable model is the cluster model, according to which any single crystal, when heated to pre-fusion temperatures, breaks down into clusters separated by amorphous layers of atoms. With increase in temperature, the thickness of the amorphous layers increases, and at the moment of fusion, rupture of the bonds between the clusters takes place. X-Ray diffraction has shown[40] that lead particles with $r \cong 10$ nm on fusion break down to give clusters with an edge length approximately seven times the lattice parameter; with increase in the temperature of the melt by 300 K, the cluster dimensions decrease by a factor of only 1.5, and the structure of the gas is acquired only at the temperature of the liquid–vapour transformation.

The size dependence of diffusion in small particles has been studied.[42,43] A relationship has been established between the activation energy of diffusion θ and the melting point of the substance T_m: $\theta = \alpha T_m$.[44] If it is assumed that this relationship is preserved for a given substance in the UD state, that is that the relationship $\theta_r = \alpha T_r$ is also applicable for particles with radius r, then eliminating the factor α gives $\theta_r = \theta T_r/T_m = \theta - \theta\Delta T/T_m$, and the diffusion coefficient in a particle of radius r will be

$$D_r = A\exp\left(-\frac{\theta_r}{kT}\right) = A\exp\left(-\frac{\theta}{kT}\right)\exp\left(\frac{\theta}{kT}\frac{\Delta T}{T_m}\right) = D\exp\left(\frac{\theta}{kT}\frac{\Delta T}{T_m}\right)$$

The experimental values of the melting points of the particles should be substituted in this equation. Since $\Delta T = T_m - T_r$ increases with decrease in the particle size, D_r also increases, and for dimensions of 10 nm it differs from the diffusion coefficient D in the macro-phase by several orders of magnitude.[43]

4. The Energy Saturation and Reactivity of a Medium

A very important characteristic of UD media is their high chemical activity. This is also related to the high energy saturation of dispersed particles, in particular due to the contribution of the surface energy. Thus the equilibrium constant in a closed system is given by the expression[45] $K_e = \exp(-\Delta\Phi^0/RT)$, where the change in the Gibbs potential in the standard state is

$$\Delta\Phi^0 = \Phi_2^0 - \Phi_1^0 = \sum_j \nu_j^1\Phi_{Bj}^0 - \sum_i \nu_i\Phi_{Ai}^0$$

This equation is applicable for equilibrium with respect to the reaction

$$\sum_i \nu_i A_i \rightleftarrows \sum_j \nu_j^1 B_j$$

for given P and T. If the starting materials and products are dispersed, the change in the thermodynamic potential is:

$$\Delta\Phi = \Delta\Phi^0 + \sum_j \nu_j^1\Delta\Phi_j^1 - \sum_i \nu_i\Delta\Phi_i$$

where the summation is carried out over the dispersed reagents. Recalculation to one dispersed particle of n atoms gives $\delta\Phi = \alpha\sigma\nu^{2/3}n^{2/3}$. It is assumed that the reaction is forbidden under standard conditions ($\Phi_2^0 > \Phi_1^0$). If in the dispersed state

$$\Phi_2^0 + \sum_j \nu_j^1\Delta\Phi_j^1 < \Phi_1^0 + \sum_i \nu_i\Delta\Phi_i,$$

then the reaction becomes possible, and the equilibrium constant of the reaction can be calculated from the equation

$$K_e = K_e^{(\infty)}\exp\left[\left(\sum_i \nu_i\Delta\Phi_i - \sum_i \nu_j^1\Delta\Phi_j\right)/RT\right]$$

When the reaction products are more highly dispersed than the starting materials, the entropy factor will facilitate an increase in the displacement of the process towards the formation of the products, since $\Delta\Phi^0 = \Delta H^0 - T\Delta S^0$.

As a result of the extremely high reactivity of UDP, they react even with inert gases. On the freshly formed surfaces of finely divided solids[46] there is appreciable irreversible adsorption not only of oxygen, nitric oxide, and the products of the dissociation of the liquids in contact with it, but also of inert gases at ordinary pressure and temperature. The gas molecules form strong bonds with the surfaces of the solid particles; the bond energy, estimated from thermal data, is 2–4 kJ mole^{-1}.

The passivation of metals by inert gases is possible in the cold plasma of a glow discharge.[47] For example, the simultaneous bombardment of an aluminium surface by argon and hydrogen ions from the plasma leads to the irreversible penetration of the atoms of these gases not only into the surface layer (5–10 nm) but also into the bulk of the metal, with the formation of a metastable metal–inert gas substitutional solid solution. The concentration of absorbed argon may reach several percent.

It has been established experimentally that the limiting concentration of dissolved argon in aluminium c_0 is 0.3 at.% at 400 K. At a higher concentration, the metastable solution breaks down with the formation of gas-filled bubbles. The lattice parameter increases practically linearly with increase in the inert gas concentration from 0.40496 nm for pure Al to 0.40533 nm for Al containing 0.3 at.% Ar. If this macroscopic solution is described in the regular approximation and it is assumed that the free energy of argon in the solution is equal to that of the argon ions, then at $T = 400$ K and $c_0 = 0.003$ the energy of mixing ΔH is 1.5×10^6 J g-atom^{-1}.

If the solution is a system of small particles, the equilibrium concentration is increased. Using the Ostwald–Freundlich relationship and assuming that the concentration of Ar in the macroscopic solution is 0.003 at $T = 400$ K, and that the surface tension of the macroscopic solution–gas boundary is ~1 J m^{-2}, gives for particles with dimensions of 10, 3, and 2 nm, the argon concentration values 0.54, 2.20, and 6.10 at.% and the values of the excess energy of solution 0.76, 3.66, and 8.10 respectively in units of $\Delta H/\Delta H_m$, where $\Delta H_m = 10.68$ J mole^{-1} is the heat of fusion of aluminium. Thus the solution is formed with a huge expenditure of energy. On its relaxation (breakdown), this excess energy of mixing will be liberated, and at the lower limit of the UDM it may be appreciably greater than the heat of fusion of aluminium. In Ref.48, tablets (diameter 6 mm and height 1.2 mm) were compressed and heated at a rate of ~200 K min^{-1} in an inert gas atmosphere (under a pressure of 0.13 Pa) from powders obtained by the electrical explosion of wires ($r = 0.03$–1.3 μm). At 720–820 K the tablet of copper powder began to glow brightly, and its temperature rose to 1200 K. The temperature of the aluminium tablets increased spontaneously to 940 K, which corresponds to the melting point. Thus for powders with the degree of dispersion indicated, the excess energy is sufficient to maintain the self-propagating process of sintering and even fusion.

A whole series of papers describe the experimental observation of an increase in the chemical activity of energy-saturated media. It has been reported[49] that in two-layer oxide hetero-structures, reactions of the type

$$MgO + Nb_2O_5 \rightarrow MgNb_2O_6$$

take place spontaneously at temperatures 800–1000 K lower than the usual temperatures for the reactions in the massive state. Many examples from the work of Boldyrev and co-workers have demonstrated the activation of solid-phase reactions under the influence of mechanical subdivision,[50] a shock wave,[51], X-rays,[52] and a stream of protons.[53] Finally, recent studies have revealed the high biological activity of highly dispersed metal powders at all levels, from the general indices of the metabolism of the organism to the influence on the activity of individual biological systems and biomacromolecules.[54,55] The antimicrobial activity of various metal powders has been established. Progress in this field is being held up by the lack of satisfactory methods for introducing the metals into the organism. A possible solution is the introduction of the required metals into the organism as UD powders, particularly since their activity increases with decrease in size. This topic lies outside the scope of the present review, however, and will not be discussed in detail here.

III. METHODS FOR OBTAINING ULTRADISPERSED POWDERS OF METALS AND COMPOUNDS

1. Mechanical Methods of Dispersing Solid Metals

Ultradispersed powders can be obtained by the mechanical dispersal of solids, the decomposition, precipitation, and reduction of chemical compounds, and the condensation of metal vapours. A combination of these methods is often used.

In powder metallurgy, coarsely dispersed materials are often obtained by mechanical sub-division in ball, rod, or other mills or in disintegrators, [56] and also by electrohydraulic impact. When a certain degree of dispersion has been achieved, however, a dynamic equilibrium is established between the processes of dispersal and coagulation of the particles. To obtain particles with micron dimensions it is necessary to carry out the sub-division at very low temperatures, at which the material is more brittle, [57] to use ultrasonic dispersal, [58] or to add surface-active substances, which lower the surface energy and strength of the particles.

Sputtering of melts in liquid or gas streams, and ultrasonic [59] and other methods can also be used to obtain powders, but in these cases the products are coarsely dispersed.

The above methods can apparently be used only as an intermediate stage in the production of UD powders. Ultrasonic treatment can be applied to prepared UDP (to break down conglomerates, for mixing, and to produce more compact pressings).

There is however a form of mechanical treatment which creates conditions both for the synthesis of the desired products (diamond) and for their dispersal, namely the action of a shock wave. [60] Diamonds are obtained by the shock-wave treatment of mixtures of graphite and metals at 20–40 GPa and a shock-wave duration of 10–20 µs. The structure and composition of the resulting powders have been studied. [61] The average particle size of the diamonds was ~4 nm.

2. Physical Methods of Obtaining UD Powders Based on Volatilisation and Condensation Processes

The simplest and most natural method for obtaining UD metal powders is by volatilising the metals and condensing their vapours. This method was used to obtain UDP in early studies. [62] Assemblies using the volatilisation–condensation principle may differ in the method of introducing the material to be volatilised, the method of introducing the energy required to volatilise the metal, the nature of the working medium, the organisation of the condensation process, and the system for collecting the powder.

The metal is either volatilised from a crucible or fed to the heating system in the form of a powder, wire, or stream of liquid, through special devices.

Energy can be supplied to the metal to be volatilised through a conductor, [63] by high-frequency induction heating[64] or superhigh-frequency currents,[65] by electric-arc discharge in a plasma, [66] by a laser light flash, etc.

The processes of volatilisation and condensation may take place in a vacuum, in a stationary inert gas, or in a stream or gas (in particular in a plasma stream).

In the production of UD powders, the condensation process is the decisive stage. The physical principles of the theory of the condensation of metals is fairly well developed, [67,68] and methods have been proposed[67,69,70] for calculating the particle size distribution of metal aerosols. The numerical solution of the equations of the kinetics of bulk condensation for this model has been carried out: [70] the vapour–gas mixture in the condensation zone moved in a channel with a constant cross-section of 118.7 mm^2 at a constant velocity of 150 m s^{-1}, the axial temperature gradient due to cooling of the stream was 200 K min^{-1}, the pressure in the channel was constant and equal to atmospheric pressure, and the boundary layer was not taken into account; the argon consumption was 3.5 m^3 h^{-1} (6.24 kg h^{-1}), and the consumption of tungsten powder volatilised 2 kg h^{-1}. These values of the parameters correspond to those of a real assembly. The kinetic analysis showed that it is theoretically possible to obtain tungsten powder with an average particle size of 3–5 nm (without allowance for coagulation). The length of the coagulation zone (90 mm) is much less than the length of the nucleation zone (~4 mm); this makes it possible to protect the powder formed from coagulation, for example by removing it from the condensation zone.

Methods of condensation have been discussed in detail. [71] The vapour–gas mixture at a temperature of 5000–10 000 K can simply be passed into a chamber of large cross-section filled with a cooled inert gas, in which condensation takes place. In improved assemblies, two coaxial streams are passed into a channel; the inner axial stream contains the vapour–gas mixture, and the outer annular stream contains a cold inert gas. As a result of turbulent mixing, the temperature of the metal vapour is lowered, the supersaturation increases, and rapid condensation takes place. The width of the condensation zone in this assembly changes along the longitudinal coordinate, however, and this gives a broad particle size distribution function. Nevertheless, detailed analysis and allowance for the characteristic features of the turbulent mixing of non-isothermal coaxial streams in a channel[73] makes it possible to decrease considerably the thickness of the temperature layer and to obtain UDP with a narrow fractional composition. UDP of copper, aluminium, iron, nickel, and other metals have been obtained in this way in a laboratory assembly. [71] The average particle size of the powders obtained was 7–20 nm at a production rate of 40–50 g h^{-1}, depending on the material and the operating conditions.

If the vapour–gas mixture is directed into a channel with a cooled wall, hydrodynamic, temperature, and concentration boundary layers are established at the surface of the channel. Under turbulent conditions, the thickness of the boundary layer and hence of the condensation zone is proportional to the longitudinal coordinate to the power 0.2. [71] The resulting particles, under the influence of thermophoresis forces, are displaced across the boundary layer to the wall. The temperature gradient in the boundary layer (~10^5 K m^{-1}) is higher than in the layers of the stream, and this makes it possible to obtain particles with smaller dimensions (less than 1 µm). The particles settling out, however, accumulate on the wall surface and partly coagulate and cake to form agglomerates. The growth of the layer of particles on the wall of the channel increases the thermal resistance of the layer and the temperature of the outer layer, and this in turn leads to sintering of the particles with the formation of a crust and overgrowths. Special methods of cleaning the surface have to be used to prevent this phenomenon.

The most favourable conditions for the condensation of metal vapours (to obtain UD powders with a narrow particle size distribution) are apparently produced on adiabatic expansion in a Laval nozzle. [71,72] With sufficiently rapid expansion of the mixture, a temperature gradient of

$\sim 10^8$ K s^{-1} is created,[13] and the vapour of the metal (for example aluminium) condenses almost instantaneously to give UDP with an average particle size of 50–60 nm. The temperature of the walls of the nozzle should be greater than the melting point of the metal, to avoid the deposition of metal particles on the wall and the production of a metallic crust.

The UDP obtained are usually collected on special filters or by centrifugal deposition. In some assembles, the particles are either deposited on a rotating drum or endless belt, after which the surface is cleaned with a scraper, or trapped in a liquid film.

3. Chemical Methods for Obtaining UD Powders

Chemical methods include precipitation, the reduction of oxides and other compounds of the metals, and thermal decomposition. The chief condition for obtaining dispersed powders by chemical methods is that the reaction should take place at a distance from equilibrium, with a high rate of formation of the nuclei of the new phase, combined with a low rate of their growth. These conditions are ensured by selecting a temperature at which the chemical reaction takes place sufficiently intensively, but transfer through the gas phase is still retarded.

The deposition is carried out in a solution, a stream of gas, or a plasma. For example, titanium dioxide is obtained by precipitation as a result of the hydrolysis of titanyl sulphate with heating. The fresh precipitate is amorphous. Transformation to the rutile structure is achieved by subsequent heating to 1000–1300 K.[74] Methods for obtaining powdered iron, cobalt, nickel, and alloys of palladium have been described (see Ref.71 for bibliography). The particle size of these powders varies from 5 nm to 3 μm.

Oxides and halides are usually reduced using hydrogen or carbon monoxide. Powdered iron, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten with an average particle size of 0.1 μm have been obtained by this method at 750–1600 K.[75]

Powdered nickel, iron, chromium, copper, etc. are obtained by the thermal decomposition of the carbonyls, formates, oxalates, and other compounds at 500–700 K. These methods have been reviewed in detail.[7,74]

General unsatisfactory features of methods for obtaining metal UDP by low-temperature processes are the formation of comparatively large particles (0.03–10 μm), a wide particle size distribution, a high concentration of impurities in the powder, and a complex, multi-stage, non-universal technology. In a number of cases, however, the large-scale production of powders can be organised using these processes.

A significant increase in the degree of dispersion of the powders can be achieved by carrying out the process at high temperatures, in particular in a low-temperature plasma generated by an arc or induction discharge. This method can be used to obtain practically all refractory carbides, nitrides, borides, oxides, etc., and also more complex compounds. UD titanium nitride powders with a particle size of <0.5 μm are obtained by reducing the chlorides with hydrogen in a flux of nitrogen plasma.

Thermodynamic calculations for the systems M–Cl–H–N, where M = Ti, Zr, or Hf, show that at the stoichiometric ratio of the original components of the reaction

$$2MCl_4+4H_2+N_2=2MN+8HCl$$

the equilibrium throughout the temperature range (400 to 3500 K) is characterised by the presence of chlorides, so that the degree of transformation of MCl_4 into MN is slight, but a combined excess of hydrogen and nitrogen ensures a nitride yield of 100% over a wide temperature range.[12] The combined reduction of $TiCl_4$ and thermal decomposition of hydrocarbons in a nitrogen plasma is used to obtain titanium carbide nitrides which in the composition range from $TiN_{0.98}$ to $TiC_{0.4}N_{0.6}$ form single phases and consist of a series of solid solutions of carbon in titanium nitride with the NaCl structure. The average particle size of these powders is ~50 nm.[76]

The carbides of titanium, zirconium, hafnium, vanadium, tungsten, and other metals with an average particle size of 0.01–0.1 μm have been obtained in the plasma of an arc discharge using the corresponding metal chlorides and hydrocarbons as starting materials.[77,78]

UD copper powder has been obtained[81] by reducing copper chloride with hydrogen in the stream of argon plasma of an electric-arc discharge. A thermodynamic calculation for the Cu–Cl–H system showed that it is possible to obtain copper in a yield close to 100% in the temperature range 500–1800 K with more than ten-fold dilution of the system with hydrogen, relative to the stoichiometric quantity. The assembly gave copper powder with a particle size <0.1 μm and a relatively narrow particle size distribution.

The reduction of nickel monoxide in a high-enthalpy stream of gas obtained by the complete oxidation of propane by air:

$$C_3H_6+1.5\,O_2+5.64\,N_2=3\,CO+4\,H_2+5.64\,N_2$$

has been studied.[82]

Thermodynamic analysis showed that in a 1.2-fold excess of the reducing agent in the temperature range 800–6000 K, complete reduction of the oxide to the metal is achieved. The experiments gave nickel powder with an average particle size of 0.1–0.4 μm, containing 0.2–3% carbon and 1.5–6% oxygen.

Silicon carbide powders can be obtained from quartz sand and a propane–butane mixture[79] or from a mixture of silanes and halogen derivatives of hydrocarbons in a hydrogen plasma at 2800–3800 K. The average particle size is 0.05 to 0.02 μm.

UDP of tungsten have been obtained by reducing tungsten trioxide in an argon–hydrogen plasma.[80]

An unsatisfactory feature of thermal decomposition and reduction methods is the low selectivity of the process; the reaction product usually consists of a mixture of the desired product and other compounds.[14]

Overall, however, assembles with a low-temperature plasma at present provide one of the most efficient, productive, and universal means of obtaining UDP of metals and compounds.

4. The Electrical Explosion of Wires

One version of the volatilisation–condensation method involves the production of UDP by the electrical explosion of wires. This method is dealt with separately because of its practical importance.

In the electrical explosion of wires (EEW), the materials of the wire breaks down under the influence of a powerful current pulse; part of the material of the wire may volatilise, while the rest is scattered as liquid droplets.[83] As a result of volatilisation at the expense of condensation in the stream of rapidly expanding vapour, particles with very small dimensions are formed, but the solidified droplets give larger particles. The ratio of these components depends on the nature of the breakdown of the wire, which is determined by the process used to introduce the energy into the wire.

The quantities characterising the electrical explosion of wires are functions of the parameters:[84]

$$E = CU_0^2 n^{-2} d^{-4} Z^{-1},\ \lambda = l n^{-1} d^{-2} Z^{-1},\ \nu = L^{1/2} C^{1/2} d^{-1}$$

where l is the length, d the diameter, and n the number of the exploding wires, Z the wave resistance, L the inductance, C the capacity of the circuit, and U_0 the initial voltage at the condenser. The parameters of the explosion are selected using these variables.

The results of the study of copper powders obtained at an inert gas pressure of 200 Pa have been described.[63] The size of the spherical copper particles depends to a significant extent on the density of the energy introduced and the rate of its introduction. It is possible to obtain a powder with a maximum size distribution in the region of 20 nm for copper exploded in air, or in the region of 50 nm for aluminium in argon.

5. Freeze Drying

Ultradispersed powders of metals and compounds can be obtained by freeze drying. The starting materials, in particular metal salts, are used to prepare a solution with the required composition, which is rapidly frozen by spraying into a chamber containing a cryogenic medium. The pressure of the gaseous medium above the frozen granules is then decreased until it is lower than the equilibrium pressure for the multi-component system formed on cooling, and the material is heated with continuous evacuation to sublime the solvent. The product consists of very fine porous granules with identical composition. Heating the granules in air gives the oxides, reduction gives the metal powders, and selective reduction gives a mixture of the oxides and the metals. The UD compositions Pb–10% MgO, W–S, W–25% Re, $Cu-ThO_2$, Cu–W, $NiZnFe_2O_4$, etc. with a particle size of 10–60 nm have been obtained in this way.[85,86]

The reduction of ammonium paratungstate in solution by hydrogen gives a finely dispersed tungsten powder with a particle size of 0.2–0.8 μm, and the product acquires a completely new structure.[87] Ammonium paratungstate has several crystalline hydrated forms, each of which gives a characteristic X-ray diffraction pattern. When the paratungstate obtained by freeze drying was examined by X-ray diffraction, however, no diffraction lines were observed.

Sub-micron nickel powders are obtained by this method from solutions of nickel chloride and nitride.

IV. ENERGY-SATURATED MEDIA AS MATERIALS OF PRESENT-DAY TECHNOLOGY

1. Materials with an Ultradispersed Structure—A Unique Form of Composite Material

Attempts to eliminate the gap between the requirements to be satisfied by constructional materials for present-day technology and the possibilities provided by the usual alloys of materials science are being made by developing and applying composite materials.[24] The complexity of this problem lies in the fact that elements of different kinds (for example metal and non-metal), combined in the same composite material, must function as a single whole. For a long time these difficulties could not be overcome, so that in the past, materials consisting of one substance were preferred.

Composite materials may be of three main types: metal + metal; ceramic + ceramic; and metal + ceramic. The components either do not react, or react with one another during use. In the first case the system is a purely mechanical system, whose behaviour under working conditions can be predicted from mechanical data with allowance for the scale factor. In the second case, the components of the composite materials react to form a new product at the interface. This practically always takes place, since during use the materials are subjected to high temperatures and pressures and other influences. For inorganic materials used at sufficiently high temperatures, the first case need not be considered.

The reaction "within" the composite material may give chemical compounds corresponding to the complete range of possible oxidation states of the metal, including sub-compounds, complex compounds, compounds formed by ceramic + ceramic and metal + metal (intermetallic compounds) combination, and also phases of variable composition of the solid solution type. Thus the "spectrum" of components of a composite material is complicated considerably when the corresponding material starts to be used at high temperatures. This makes it difficult to calculate accurately the behaviour and capacity of the material at different stages of its use, and its examination is usually restricted to the determination of the dependence of the properties, in particular the strength characteristics of the material, on the intensity of the reaction with time. These phenomenological data have now been collected for a whole range of composite materials, and their amount is increasing rapidly. The generalisation of this experience still lags behind practice. A tendency to move to the "molecular level" in the examination of the mechanisms of the reactions of the components of composite materials is gradually being observed, in spite of the considerable difficulty of these questions.

It should be noted, in particular, that the view that the composition of the products of the reaction in composite materials is determined by data from the corresponding equilibrium diagrams cannot be fully accepted, since composite materials are generally non-equilibrium systems. Thus kinetics must be added to present-day methods for their physicochemical analysis. Composite materials are "living" systems, and kinetic questions become fundamental in their study during use. The equilibrium diagrams in the case being considered are of major importance if they are constructed from data obtained in experimental studies with allowance for kinetics. The question of the importance of obtaining "kinetic" equilibrium diagrams is not new,[88] but it has not found extensive practical application. The possible reason may be that up to the present, physicochemical analysis has been applied chiefly to substances as such, when there has been no particular need to study the kinetics of the corresponding processes. Moreover, in the examination of composite materials it is necessary to take account of the degree of dispersion of the starting material and the products formed when the materials are used.

It is usually assumed that composite materials are artificial systems made up of the corresponding macro-components, namely the matrix, which is a compact material (metal or ceramic) of any dimensions, and the reinforcing material, in the form of fibres or filaments, ceramic or metallic, and best of all in the form of single crystals. Since a sharp boundary cannot be drawn between macro- and micro-states, the concept of composite material can apparently be extended to include in this category materials having components with atomic or molecular degrees of dispersion, placing arbitrary boundaries between individual groups.

It is appropriate to divide each of these three types of composite material into three groups, in which the components differ in their degree of dispersion.

1) Composite materials made up of two parts ("blocks") of any dimensions, each of which has independent functions. In this case the area of contact between the blocks is negligibly small compared with the blocks themselves, and at high working temperatures (not exceeding their melting points) the behaviour of the corresponding composite material can be regarded as a function of the behaviour of its component parts, and the "events" at the interface are of secondary importance, the interface functioning only as a means of holding the blocks together.

2) Composite materials in which the degree of dispersion of the reinforcing particles is relatively high: fine single-crystal filaments, short (1–5 mm) fibres, and fine crystals. Here, the components cannot behave independently, and the mass of the interphase formations may be comparable with that of the original components. The behaviour of this most widely encountered classical type of composite material ($Al + Al_2O_3$; $Mg + MgO$; etc.) must be examined in a known temperature range as a system which is the usual object of physicochemical analysis.

3) Composite materials at the level of mixing of components with atomic or molecular dimensions. These are ordinary chemical compounds of the type AB, AB_2, A_2B, etc., up to double salts and complex compounds, and also phases of variable composition. Materials with these components are not usually regarded as composite materials, but in principle this is not quite correct, since there may also be external factors influencing the material (for example radiation, defect-forming influences), when its component atoms or molecules behave "independently" and influence the working properties of the material.

The proposed classification may possibly be disputed, but it covers all types of composite material, if they are classified according to the particle size of the components. Moreover, account must be taken of the fact that at sufficiently high temperatures (for example close to the melting points of the components), their mutual diffusion will take place so rapidly that a composite material of type 2 begins to function as a composite material of type 3. It is always necessary to take into account the extent to which this transformation of one type of material into another is permissible from the viewpoint of the application of the composite material.

2. The Relationship Between the Energy Saturation, Structure, and Mechanical Properties of Materials

The characteristic feature of ultradispersed particles discussed in the previous sections also appear in compact materials with an ultradispersed structure. In this case the degree of dispersion is determined by the average dimensions of the defect-free regions (structural fragments) and the angles of disorientation between them. Here, the relationship between the ultradispersed structure and the physicomechanical properties of the materials is of the greatest importance.

In these materials it is possible to distinguish three levels of structural organisation:[21] granules with dimensions of 10^3–10^4 nm, angles of disorientation 1–90°; sub-granules with dimensions of 50–10^3 nm, angles of disorientation 5′–3°; and blocks with dimensions of 3–100 nm, angles 5′–5″. The energy saturation of a structure of this kind depends on the dimensions of the elements of the structure and the energy of the interfaces. The energy of the interfaces, calculated by the Shockley–Read method, for example for nickel, varies from 0.0014 J m^{-2} ($\theta = 30''$) to 1.1 J m^{-2} ($\theta = 57°$).[21]

Analogous calculations of the excess values of the chemical potential for gold show that for dimensions of the structural fragments of 4.5 nm and large-angle interfaces between them, the state of the structural fragments corresponds to the state of the macro-system at the melting point, and that for dimensions of ~10 nm and large-angle interfaces it corresponds to the state of the macro-system at a temperature of 0.6 T_{fusion}. Since at this temperature relaxation processes (of the crystallisation type) take place actively in metals, a dispersed system with these parameters will not apparently be stable.

For low-angle boundaries, an analogous state is reached at structural fragment dimensions of ~3 nm. It is evidently possible to speak of a limiting attainable level of dispersion of a polycrystalline system.

Accordingly to the familiar Oding diagram, the greatest strength is shown either by materials with a low density of dislocations (single crystals) or materials with a dislocation density of 10^{13}–10^{14} m^{-2}. The strength properties of metals are influenced not only by the density of dislocations, but also by the nature of their distribution in the volume. Distribution of the dislocations in the form of networks of block boundaries is thermodynamically favourable. Assuming that all the dislocations lie at the boundaries between the blocks, the size of the blocks L is related to the density of dislocations ρ by the expression:[89]

$$L = (a/\rho)^{1/2}$$

where a is a parameter of the order of 1, defining the degree of regularity of the distribution of the dislocations. For $\rho = 10^{15}\,m^{-2}$, the dimensions of the blocks lie in the range 4–5 nm.

The relationship between the structure and the strength characteristics is given qualitatively by the Hall–Petch relationship,[90] according to which the strength of a metal is proportional to $L^{-1/2}$, where L is the size of the granules for materials with a coarsely granular structure, and the size of the blocks for materials with highly developed fragmentation of the structure.

By changing the sub-structure of the materials (the size of the structural fragments and the angles of disorientation), it is possible to control their physicomechanical properties.[90,91] For example, the strength of U-8 steel increases from 1.4 GPa to 2.8–3.2 GPa with decrease in the size of the structural fragments from 30 nm to 10 nm. The yield point of TsM-6 molybdenum alloy increases from 400 MPa to 750 MPa with decrease in the particle size from 160 μm to 1 μm. With decrease in the size of the granules of the sub-structure, the impact strength also increases. Thus for 45 steel it changes from 0.62 kJ m^{-2} to 1.5 kJ m^{-2} with decrease in the size of the granules from 60 μm to 6 μm.

An important feature is that with the increase in strength, a sufficient reserve of plasticity is retained, since the temperature of cold brittleness is lowered. For example, for molybdenum it is lowered from 600 K to 415 K with decrease in the size of the granules from 7.3 μm to 1.2 μm.

The temperature of the transition from viscous to brittle breakdown (the temperature of cold brittleness) is a structure-sensitive property, and decreases with decrease in the size of the elements of the sub-structure.[23] The formation and growth of cracks of critical dimensions in an UD material is hindered because of the small size of the structural fragments and the presence of a large number of boundaries, so that the breakdown viscosity of the UD material is increased.

Lowering the temperature of cold brittleness and increasing the breakdown viscosity are important aims for most constructional materials, particularly refractory materials, intermetallic compounds, and metal–ceramics. The possibilities provided by traditional methods (metallurgical, thermal, thermomechanical) in this area have been practically exhausted. To solve the problems of improving further the physicomechanical properties of materials it is necessary to look for new methods of producing ultradispersed structures.

3. The Production of Highly Dispersed States in the Synthesis of Titanium Carbide Under Bulk Combustion Conditions

The mechanism of the formation of a dispersed structure in the synthesis of titanium carbide under non-isothermal conditions can be considered. It has been shown[17,91,94,95] for the Ni–C, Al–Si, and other systems that the presence of ultradispersed components in the original system gives metastable equilibrium diagrams. Thus the temperature of eutectic formation in the Zr–C system is lowered by 500 K when the form of carbon used is coke with an excess energy of about 8.4 kJ mole^{-1}.

The Ti–C system has been studied.[92] It contains an intermediate titanium carbide phase (subsequently denoted σ). The equilibrium diagram can be divided into two regions, Ti + σ and σ + C. The thermodynamic potentials in the left-hand and right-hand regions will have the form:

$$\Phi^{\mathrm{Ti}+\sigma}=(1-x)\Phi^0_{\mathrm{Ti}}+x\Phi^0_{\mathrm{C}}+(x/x_0)\Delta\Phi^\sigma,$$
$$\Phi^{\sigma+\mathrm{C}}=(1-x)\Phi^0_{\mathrm{Ti}}+x\Phi^0_{\mathrm{C}}+[(1-x)/(1-x_0)]\Delta\Phi^\sigma$$

The thermodynamic potential of the σ-phase can be estimated by the published method:[93]

$$\Delta\Phi^\sigma=x(1-x)W_0+(1-x)(1-2x)W_1+x(1-2x)W_2+$$
$$+RT\{A_1x+A_2x^2+(1-x)\ln[(1-x)/(1-2x)]-x\ln[x/(1-2x)]\}$$

where for titanium carbide $A_1 = 0.62$, $A_2 = -0.32$, $W_0 = -368 \times 10^6$ J kmole^{-1}, $W_1 = 117 \times 10^6$ J kmole^{-1}, $W_2 = 92 \times 10^6$ J kmole^{-1}. Substituting gives $\Delta\Phi^\sigma = (92 \times 10^3 - 1.9T)$ J kmole^{-1}.

The liquid phase can be described in the approximation of regular solutions

$$\Phi^L=(1-y)\Phi^L_{\mathrm{Ti}}+y\Phi^L_{\mathrm{C}}+RT[y\ln y+(1-y)\ln(1-y)]+y(1-y)\Delta L$$

where ΔL is the interaction parameter in the liquid solution,

$$\Phi^L_{\mathrm{Ti}}=\Phi^0_{\mathrm{Ti}}+\Delta H_{\mathrm{Ti}}(1-T/T_{\mathrm{Ti}}),\quad \Phi_{\mathrm{C}}{}^L=\Phi_{\mathrm{C}}{}^0+\Delta H_{\mathrm{C}}(1-T/T_{\mathrm{C}}),$$

and the temperatures and enthalpies of fusion of the components have the values $T_{\mathrm{Ti}} = 1940$ K, $T_{\mathrm{C}} = 4000$ K, $\Delta H_{\mathrm{Ti}} = 15.47 \times 10^6$ J kmole^{-1}, and $\Delta H_{\mathrm{C}} = 104.5 \times 10^6$ J kmole^{-1}.

For simplicity it will be assumed that the homogeneity range extends to a line around $x = 0.5$; the formation potential $\Delta\Phi^\sigma$ at the point of congruent fusion is related to $x = 0.5$; the range of solubility of titanium in carbon (α-solution) and the influence of pressure are neglected, and the data on the fusion of carbon are taken for $P = 10^7$ Pa.

Using the condition $\Phi^{\sigma+\mathrm{C}} = \Phi$ on the right-hand eutectic of the equilibrium diagram ($x = 0.643$, $x_0 = 0.5$, $T_e = 3049$ K) gives $\Delta L = -258.6 \times 10^6$ J kmole^{-1}. The lowering of the right-hand eutectic as a result of the dispersal of carbon can now be estimated. In this case it is necessary to add to the left-hand side of the condition $\Phi^{\sigma+\mathrm{C}} = \Phi^L$ the term $\Delta H_{\mathrm{excess}}(x - x_0)/(1 - x_0)$ reflecting the contribution of the excess energy. For $x - y$ this gives the equation

$$[(1-x)/(1-x_0)]\Delta\Phi^\sigma+[(x-x_0)/(1-x_0)]\Delta H_{\mathrm{excess}}=(1-x)\Delta H_{\mathrm{Ti}}(1-T/T_{\mathrm{Ti}})+$$
$$+x\Delta H_{\mathrm{C}}(1-T/T_{\mathrm{C}})+RT\{x\ln x+(1-x)\ln(1-x)\}+x(1-x)\Delta L$$

By specifying a series of values of $\Delta H_{\mathrm{excess}}$ and looking for the minimum $T = T(x)$ it is possible to find the positions of the eutectic for different carbon materials (CM). The estimates give downward temperature displacements of the right-hand eutectic of 540 K for coke, 1200 K for carbon black, and 1800 K for "amorphous" carbon, with a simultaneous displacement to the right along the concentration axis.

Since the carbide phase formed is also dispersed, it is also possible, by estimating the excess energy of the σ-phase and making use of the condition $\Phi^\sigma = \Phi^L$, to determine the decrease in the temperature of congruent fusion and then to construct the entire metastable equilibrium diagram, as described in Ref.91, including the left-hand side (with allowance for the degree of dispersion of titanium).

The characteristic features of the M–C diagram determine the mechanism of the reaction of fine-crystalline mixtures of a metal and CM. In the reaction of Ti with imperfect forms of carbon, nuclei of the carbide phase, which will give the titanium–carbide eutectic, are formed first at the Ti–C interface. Because of the dispersal of Ti and the carbide, the temperature of the titanium–carbide eutectic will be lowered. The metal, penetrating into the channels of the CM, accumulating in the micro-pores, and reacting with carbon, gives new TiC nuclei, and Ti and TiC give a metastable eutectic. The front of this eutectic is displaced towards the imperfect CM, leaving perfect forms behind it, that is "processing" of the CM takes place. When $T \geq T_e$ for the right-hand metastable eutectic is reached, as a result of spontaneous heating of the mixture, the same processing of the CM begins, but now with the carbide–carbon eutectic, with simultaneous precipitation of the carbide phase. This stage determines the yield of carbide. These processes are based on the phenomenon discovered by Elyutin and co-workers.[16] There are many reaction channels, but the system tends to lower its energy, so that the basic reaction is the processing of the imperfect forms of CM.

Since the new phase appears on the metastable equilibrium lines, it is strongly supercooled, as it were "self-quenching" takes place, and an ultradispersed structure is produced because of the retardation of the relaxation processes at low temperatures. This method can also be used to obtain UD structures in the non-equilibrium processes of the combustion of powdered exothermic mixtures in the synthesis of intermetallic compounds, carbides with metallic bonding, and other materials.[94,20]

4. The Production of an Ultradispersed Structure in the Plastic Deformation of Titanium Nickelide

One method for the intensive treatment of solids involves a combination of high pressure and shear deformation. Available data indicate that this leads to physical and chemical processes which cannot be initiated by other methods.

The fine structure of titanium nickelide formed by the action of high pressure and shear deformation, various physicomechanical properties of the intermetallic compound, and the stability of its structure when heated have been studied.[18,96] The original specimen was a TiNi strip with thickness 200 μm, annealed at 770 K for 1 h.

Analysis of the X-ray spectra shows that the diffraction reflections become broader and merge to give a single diffuse reflection on going from the centre to the periphery of the specimens; with increase in the angle of rotation of the anvils, these differences in the structure are less clearly defined. This is due to the increase in the degree of dispersion and defect character of the structure. The dimensions of the structure are approximately 3–1.5 nm.

Electron microscope studies showed that at low degrees of deformation the granular structure of the material is close to the original structure, that is deformation takes place within the structural fragments, and the distinct boundaries between them are retained. At high deformations, dispersal takes place and the range of coherent scattering of X-rays decreases.

With increase in the deformation and pressure, the microhardness of the specimens increases and reaches 9 GPa. which is almost ten times that of the material in the annealed state.

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Energy-rich media have a number of valuable physicochemical properties, which determine the possible fields of their technological application.

Such properties of UD powders as the lowered temperatures of phase transformations, the increased coefficients of diffusion in the particles, the lowered sintering temperatures, etc. make them particularly attractive for the synthesis of materials with unique properties by sintering, reactive sintering, hot pressing, and hot isostatic pressing; for preparing pastes for low-temperature soldering and welding, etc.

The chemical activity of UDP, including biologically active materials, is finding a number of useful applications.

The properties of energy-saturated solids (metals and alloys) are equally valuable. These include increased strength, hardness, and toughness, and lowered cold brittleness threshold, for materials with an ultrafine fragmentation structure.

A number of technologies have been developed, and experience gained, in the construction and use of experimental assemblies for the production of UDP of metals and compounds. Experience has also been gained in the storage, transportation, mixing, and compaction of UDP.

All this makes the problem of the technological application of energy-saturated media in industry and the national economy of the greatest importance.

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The Thermal Theory of the Ignition of Reacting Condensed Substances

I.S.Lyubchenko and G.N.Marchenko

The processes involved in the solid-phase ignition of reacting condensed substances, taking place in the absence of mass diffusion due to temperature or concentration gradients, have been examined using a single asymptotic method. An analytical criterion for the ignition of a substance has been formulated, and a basis obtained for a universal linearisation method, which makes it possible to express experimental results statistically in the form of a linear relationship in a special system of coordinates. The question of the range of existence of non-degenerate ignition conditions has been discussed in detail. Experimental data confirming the reliability of the thermal of ignition have been given.

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I. INTRODUCTION

The study of the processes involved in the ignition of reacting condensed substances has developed extensively throughout the world in recent decades, because of their practical importance. The development of the theory of ignition originates in classical studies of the theory of thermal explosion,[1-3] summarised in a monograph.[4] The simplest model of the surface ignition of a condensed substance was first studied in Refs.5–8, where numerical integration using a computer was used to solve the non-stationary problems of the heating of the surface of a substance with an exothermic reaction taking place in the solid phase and with the Arrhenius dependence of the reaction rate on temperature.

The non-stationary thermal model of ignition adopted in these studies provided a basis for subsequent theoretical and experimental work, which has been reviewed in Refs.9 and 10 and in a recent monograph.[11] Since then, a large number of studies have been carried out, and a new asymptotic method in the theory of ignition has been developed, leading to the further development of the thermal theory and its experimental justification. It has therefore become necessary to summarise the theoretical principles of the thermal theory of ignition from a single asymptotic viewpoint. Present-day asymptotic procedures, which provide a powerful analytical method for solving boundary problems for differential equations with partial and complete derivatives, are most fully described in Refs.12–16. In the solution of problems of mathematical physics of this type, represented by the problems of the thermal theory of ignition, the asymptotic method provides a well-founded and convenient instrument of study, since the numerical values of the activation energy E and the heat Q for the chemical reactions of the ignition and combustion of known substances are fairly large.

To solve these problems, extensive use is made of approximate methods, which can be divided into four groups: 1) the critical condition method,[17-21] 2) the method of breakdown into stages,[22-25] 3) the method of successive approximations,[26,27] and 4) the method of integral relationships.[28] All these approximate methods are based on physical and mathematical simplifying assumptions about the course of the process, and not on the rigorous analytical solution of the non-linear problems of the thermal theory of ignition. At the same time it should be noted that all approximate methods are based on the same general view that the ignition process takes place in two stages: inert warm-up of the substance and progressive chemical spontaneous warm-up, ending in a "temperature explosion" at the surface at the moment of ignition. These ignition conditions have been called non-degenerate,[10] in contrast to degenerate conditions, in which the ignition process cannot develop in the warm-up and spontaneous warm-up stages. Degenerate ignition conditions can obviously lead either to "superficial burning" of the substance, at high thermal fluxes from an external source, or to the production of transition conditions intermediate between ignition and spontaneous ignition, at extremely low thermal fluxes.

None of the studies mentioned above, carried out using approximate methods, gives an answer to the problem of the range of existence of non-degenerate ignition conditions. Moreover, up to the present there has been no single definition of the criterion of ignition. Since the experimental determination and the calculation of the ignition delay time depend on the choice of ignition criterion, the arbitrary nature of this choice naturally also influences the conclusions about the agreement between theory and experiment. The moment of ignition is determined experimentally by measuring either the temperature at the surface of the substance, or the intensity of radiation, or the pressure in the system, and also by recording the behaviour of the specimen after the external heat supply is stopped. Reliable ignition takes place when the total quantity of heat liberated in the chemical reactions is greater than the heat loss. It is usually assumed that ignition does not take place if stationary combustion conditions are not established after the abrupt removal of the external heat source.[3] It has been shown,[10] however, that the calculation of pulse ignition conditions using this criterion is not a rigorously justified procedure, since this criterion was obtained by solving the particular problem of the unsymmetrical combustion of a thin slab of the reacting substance.

It should also be noted that the principle of linear universalism, which makes it possible, within the ignition model adopted, to "plot" the experimental results statistically on a straight line in a special system of coordinates, and when necessary to solve the inverse problem of determining the thermokinetic constants, has not yet been sufficiently developed.

Before proceeding to the presentation of the asymptotic thermal theory of ignition, it may be noted that in the literature[9] there are three main groups of ignition model, differing in their representation of the place where the main chemical reactions take place: 1) the model of gas-phase ignition, 2) the model of heterogeneous ignition, and 3) the model of solid-phase ignition.

In the first group of models it is assumed that ignition takes place as a result of a chemical reaction between a gaseous oxidant and a fuel vapour. This reaction is a self-maintaining heat source. Studies of the gas-phase model of the ignition of solid rocket fuels have been reviewed.[9,29] A method for calculating the ignition delay time for the case where the warm-up time of the substance is greater than the excitation time of the chemical reaction in the gas phase has been described.[30,31]

In the heterogeneous ignition model, the reaction at the phase boundary between a solid fuel and a gaseous oxidant is regarded as decisive. In the analysis of the heterogeneous ignition process it is necessary to take account of diffusion and hydrodynamic phenomena. In the particular case when the rate of the process is determined by the kinetics of the heterogeneous reaction, however, a purely thermal approach is possible.[22,23,32-37]

The solid-phase (or thermal) theory of ignition is based on the simplest (from the physical viewpoint) model of the phenomenon, in which only the processes of heat liberation and propagation in the substance are taken into account, and diffusion factors and possible phase transformations are not considered. The characteristic features of this model have been formulated,[9,10] and it is now widely used in the analysis of the processes involved in the ignition of non-volatile systems and systems difficult to volatilise.

In the present review, only the solid-phase models of ignition are analysed, for different initiation conditions.

II. THE ASYMPTOTIC ASPECT OF THE THERMAL THEORY OF IGNITION AND THE INFLUENCE OF THE MECHANISM OF HEATING ON THE BASIC REGULAR FEATURES OF THE IGNITION PROCESS

The dimensionless numerical parameters $\varepsilon = RT_0/E$, $\gamma = cRT_0^2/QE$, where T_0 is the initial temperature of the substance, c the heat capatity, and R the universal gas constant, appear in the mathematical description of the thermal model of ignition;[38-40] when $\varepsilon = 0$, because of the Arrhenius temperature dependence of the reaction rate, the chemical sources of heat become degenerate, and when $\gamma = 0$ there is no combustion of the substance in the ignition delay period, which corresponds to a zeroth-order reaction.

A natural element of the asymptotic analysis of the problems of the thermal theory of ignition is the construction of a non-stationary space–time temperature field in the substance as $\varepsilon \to 0$ ($\varepsilon \neq 0$). For this purpose, use is made of a compound asymptotic expansion, which gives a uniform approximation to the exact solution of the ignition problems both in and outside the boundary layer. Since in this case non-linear equations of a parabolic type with an exponential source are being analysed, it follows that in cases where the highest temperature is reached at the surface of the substance there is a "temperature explosion" at the surface at the moment of ignition t_*, that is there exists only a local solution of the boundary problems in the range $0 < t < t_*$. For the specific thermal model of ignition, the relationship between the rates of supply of heat from an external source of energy and from chemical reactions at the moment of ignition is calculated unambiguously. This relationship, which can be taken as a criterion of ignition, is generally easily transformed into a linear equation in a special system of coordinates and can be used to calculate the thermokinetic constants of the reaction from experimental data. In contrast to the ignition criterion, which assumes that the rates of supply of heat from the reaction and from an external source of energy are equal at the moment of ignition,[10,18,19,26,41] the asymptotic criterion in principle does not specify this equality. Other criteria, adopted in Refs. 28 and 42–47, are not sufficiently well-founded, since they were not obtained from a rigorous analysis of the corresponding boundary problems of the thermal theory of ignition. They are applicable only in a restricted range of conditions of combustion initiation.

The asymptotic analysis, together with the ignition criterion, leads to two definite inequalities, fulfilment of which determines the range of existence of the asymptote or, in other words, the range of existence of non-degenerate ignition conditions. This question has not previously been discussed in the literature, although information on the range of existence of non-degenerate ignition conditions is very necessary for experimental workers in the correct organisation of experiments and choice of initial parameters and appropriate recording apparatus. The analytical apparatus of the method of compound asymptotic expansion exists in differential[40] and integral[48] versions. The influence of the mechanism of heating of a substance on the basic regular features of the ignition process is examined below for the case of the solution of the specific problems in the thermal theory of ignition, and simple equations are given for calculating the characteristics of ignition.

1. Dynamic Conditions of Ignition of a Non-transparent Condensed Substance

For a semi-infinite solid slab and a one-dimensional thermal flux, the mathematical formulation of the ignition problem has the form:[49]

$$\left.\begin{array}{l} T_t = \varkappa T_{xx} + Qk_0c^{-1}(1-\eta)\exp[-E/RT], \\ \eta_t = k_0(1-\eta)\exp[-E/RT] \\ t=0: T=T_0,\ \eta=0;\ x=\infty: T=T_0 \end{array}\right\} \qquad (1)$$

$$x=0: -\lambda T_x = q(t);\ q>0 \qquad (2)$$

Here, T is the current temperature of the substance, t the time, x the spatial coordinate, η the degree of transformation, q the density of the thermal flux from the external source, ρ, λ, and κ the density, coefficient of thermal conductivity, and temperature conductivity of the substance respectively, and k_0 the pre-exponential factor. The other symbols were given above.

The asymptotic study of the general problem (1) and (2) has been carried out.[48,49] The chief characteristics of the ignition for the particular case $q = At^n$, $A > 0$, $n > -0.5$ are calculated using the equations:[50]

$$t_* = \left[\left(\frac{\lambda T_0}{A}\right)^2 \frac{u_*}{\varkappa}\right]^{\frac{1}{2n+1}},\quad T_* = T_0\theta_*,\quad T_i = T_*\left(1 + \frac{\theta_*}{2}\varepsilon\ln(1/\varepsilon)\right),$$
$$Q_* = \frac{At_*^{n+1}}{n+1},\quad \eta_* = 1.48\gamma\varepsilon^{-1/2}\theta_*\left(\frac{d\theta_*}{du_*}\right)^{-1/2} \qquad (3)$$

Here, the dimensionless ignition delay time u_* is determined from the transcendental equation

$$A=\left[\frac{\varkappa}{u_*(\lambda T_0)^2}\right]^n\cdot\left[1.5385\,\varepsilon^{1/2}Q\rho k_0\lambda T_0\theta_*\left(\frac{d\theta_*}{du_*}\right)^{-1/2}\exp\left(-\frac{1}{\varepsilon\theta_*}\right)\right]^{n+1/2}\qquad(4)$$

and $\theta_* = \theta_*(u_*)$ is calculated from the equations

$$\theta_*=1+\frac{u_*^{1/2}}{\delta_n},\quad \delta_n=\frac{\Gamma(1.5+n)}{\Gamma(1+n)}\qquad(5)$$

In Eqns.(3), T_* is the scale temperature, T_i the ignition temperature, Q_* the minimum energy required for ignition, and η_* the extent of the combustion in the ignition delay period. The tabulated Euler gamma-function $\Gamma(z)$ is used in Eqns.(5). Eqn.(4) gives the relationship between the rates of supply of heat from the external source and from the chemical reactions at the moment of ignition. It can be written in the form

$$At_*^n=\sigma_n\left\{\lambda\rho Qk_0\frac{RT_*^2}{E}\exp\left(-\frac{E}{RT_*}\right)\right\}^{1/2}\qquad(6)$$

where

$$\sigma_n=\theta_0^{1/4}[2.1757\,\delta_n]^{1/2},\quad \theta_0=E(T_*-T_0)/RT_*^2$$

For $n = 0$ (constant thermal flux), the expression for σ_0 has the form $\sigma_0 = 1.39\,\theta_0^{1/4}$, and with increase in the parameter n the function σ_n increases, that is $\sigma_n > \sigma_0 \cong 2.9$–$3.1$. Eqn.(6) can be used as a criterion of ignition. At the same time, in Refs.10, 18, 41, and 51, the value of σ_n is assumed to be 1. The range of existence of non-degenerate ignition conditions is determined by the inequalities[50,52]

$$A^-(n,\ T_0)\leqslant A\leqslant A^+(n,\ T_0)\qquad(7)$$

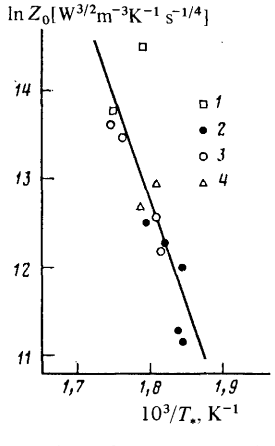

Figure 1. Determination of the thermokinetic constants of the ignition of nitrocellulose from experimental data;[50] continuous line—calculated by the least-squares method; the experimental points were obtained for the following values of n: *1*) 0.6; *2*) 1.0; *3*) 1.39; *4*) 2.8.

Eqn.(4) is readily transformed to the special form

$$\ln Z_0=\ln[2.1757\,\rho Qk_0\varkappa^{1/4}(R\lambda/E)^{1/2}]-\frac{E}{RT_*}\qquad(8)$$

where Z_0 and the scale temperature T_* are determined from the measured values of T_0, A, n, and t_* using the equations

$$Z_0=A^{3/2}T_*^{-1}t_*^{(6n-1)/4}\delta_n^{-1/2},\ T_*=T_0+At_*^{n+1/2}\cdot\delta_n^{-1}(c\rho\lambda)^{-1/2}\qquad(9)$$

Eqn.(8) is described graphically by a straight line in the coordinates $\{\ln Z_0,\ 10^3/T_*\}$. It is universal for any values of $\{A, n, T_0\}$ in the range of existence of non-degenerate conditions. By treating the experimental results by the least-squares method in the system of coordinates indicated, it is possible readily to calculate the thermokinetic constants E and Qk_0. Fig.1 gives experimental data on the ignition of nitrocellulose under dynamic conditions in a special light apparatus.[50] The least-squares method gave the values

$$\ln Z_0=56.3458-24.25\frac{10^3}{T_*},E=201\,760\ \text{J mole}^{-1},\ Qk_0=2.4932\times10^{25}\ \text{W kg}^{-1},$$

in good agreement with published data.[10]

To illustrate the effectiveness of the asymptotic method of calculating the characteristics of ignition, Table 1 compares the experimental[50] values of the ignition delay time of nitrocellulose at T_0 = 300 K with the values calculated using Eqns.(3). The agreement between these values of t_* is good. Finally, it may be noted that the influence of the relative uncertainty of the determination of σ_n on the accuracy of the estimation of t_* has been studied,[53] and it was concluded that this influence decreases with increase in n.

Table 1. Principal characteristics of the ignition of nitrocellulose by a variable thermal flux.

Experiment (Ref.50)		Calculated from Eqns.(3)-(6)				
$10^5 A$, W $m^{-2}s^{-n}$	t_*^e, s	t_*^c, s	T_i, K	Q_*, kJ m^{-2}	$10^4\eta_*$	σ_n
n = 0,6						
18.813	0.105	0.107	608.6	33.1529	1.8429	3.3894
41.146	0.0495	0.054	919.6	24.4484	1.9079	3.3902
n = 1.0						
0.9218	1.442	1.453	571.5	97.2854	1.8470	3.6029
1.0685	1.310	1.321	572.8	93.2294	1.8557	3.6033
3.1257	0.640	0.662	582.8	68.4039	1.9209	3.6063
4.6509	0.500	0.512	586.6	60.9925	1.9457	3.6072
6.4526	0.410	0.415	589.7	55.4927	1.9664	3.6079
n = 1,39						
4.7515	0.602	0.611	585.4	61.3179	2.1398	3.7900
9.8465	0.411	0.420	591.0	51.8317	2.1805	3.7913
50.28	0.179	0.181	603.9	35.5799	2.2749	3.7937
67.166	0.155	0.156	606.2	33.2798	2.2922	3.7940
n = 2.8						
25.308	0.492	0.494	592.3	45.6457	2.8152	4.2986
61.731	0.372	0.379	596.4	40.5171	2.8531	4.2995

2. The Ignition of a Transparent Substance by a Constant Thermal Flux (n = 0, A = q)

This problem requires special consideration because of its considerable methodological importance, since in this case it is possible to compare results obtained by different authors. Eqns.(3)–(6) for n = 0 lead to calculation equations for determining the characteristics of ignition, and also ignition criteria, differing considerably from those adopted in the literature. This difference is illustrated by data on the value of σ_0 used in approximate methods (Table 2).

This variety of ignition criteria obtained is related to the fact that rigorous allowance was not made for the explosive character of the change in temperature at the surface of the substance at the moment of ignition. Only the method of compound asymptotic expansions[50,54] has made it possible to obtain a well-justified ratio of the rates of supply of heat from the reaction and from the external source at the moment of ignition, and also to find the relationship $\tau_* = (t_*/t_0) = 0.4065\ \theta_0^{3/2}$, where t_0 is the adiabatic induction period of the thermal explosion at a temperature T_*.

Table 2. Comparison of different criteria for the ignition of condensed substances by a constant thermal flux.

σ_0^2	Refs.
$1.39^2 \cdot \theta_0^{1/2}$	[5, 4]
2	[43]
1	[18, 19, 28, 55]
17.64	[46]
$0.1 \cdot \pi\theta_0$	[7]
$0.5 \cdot \pi\theta_0$	[19]
$0.5 \cdot \pi^{1/2}\theta_0$	[47]
$\{[(1+0.2\theta_0^{-1})-2.67\theta_0^{-1}\lg\theta_0]+1.0424\theta_0^{-0.845}\}^{-1}$	[24]*
$[2\theta_0^2-2\theta_0+1]/1.76(2\theta_0-1)$	[25]
$\exp\{\theta_0[(1.71+38\theta_0^{-2})^{1/2}-1]-3.13\}$	[10, 46]
$0.25 \cdot \pi[1+\theta_0^{-1}\ln 2\theta_0]^{-2}$	[28]*
$0.25 \cdot \pi\theta_0^2(1+0.5\theta_0)^{-1}$ (adiabatic method)	[44]*
$0.137^2 \cdot \theta_0^{1/2}$	[21]*

*Relationship obtained by the present authors using Eqn. (18) from Ref.10.

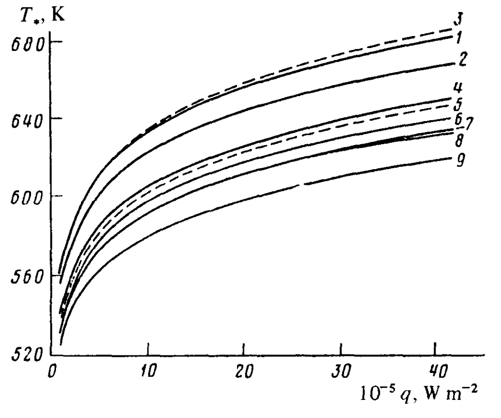

Figure 2. Dependence of the ignition temperature of nitrocellulose on q, calculated from various data: *1*) Refs.18, 19, 55, *2*) Ref.45, *3*) from Eqn.(3), *4*) Ref.7, *5*) from Eqn.(3), *6*) Ref.25, *7*) Ref.46, *8*) Ref.47, *9*) Refs.10 and 46.

To illustrate the influence of the value of σ_0 on the scale temperature T_*, calculated on the basis of the combustion criterion (6) for $n = 0$, Fig.2 gives the $T_*(q)$ relationships obtained from the data of different authors for $T_0 = 303$ K for nitrocellulose; the thermophysical and kinetic constants required for the calculation were taken from Ref.10. Since all the authors assume that $T_* = T_i$, Fig.2 gives the curve for the ignition temperature T_i (curve *3*), calculated using Eqn.(3). Curve *5*, obtained by the asymptotic method, is extremely close to curve *4*, obtained by numerical integration using a computer,[7] and curve *3* agrees fairly well with curve *1*.[18,19,55] On the whole, the discrepancy in the values of T_* obtained by different authors increases with increase in the density of the thermal flux, reaching 10%. A comparison of the values of t_* and T_* calculated by the asymptotic method with the results of the numerical solution of the problem using a computer[7] can be carried out for nitrocellulose at $T_0 = 303$ K on the basis of the data in Table 3. Good quantitative agreement is observed.

Table 3. Comparison of the results of the asymptotic and numerical solutions of the problems of ignition by a constant thermal flux.

$10^{-4} q$, W m^{-2}	8,38	41,9	83,8	209,5	419
T_*, K (Ref.7)	542	582	601	628	650
t_*, s (Ref.7)	1.564	0.0852	0.0243	0.00463	0.00132
T_*, K (Ref.54)	539	578	597	623	645
t_*, s (Ref.54)	1.522	0.0828	0.0236	0.00449	0.00128

Note. The values of T_* and t_* were obtained by numerical integration using a computer in Ref.7, and by the asymptotic method in Ref.54.

The results of the calculation of the ignition delay time using the asymptotic equations (3)–(5) and the equations obtained in Refs.28 and 56 can be compared. In Ref.56, the value of t_* was calculated using the interpolation equation

$$t_* = 0.699\ \frac{\lambda\rho c}{q^2}(T_* - T_0)^2,\quad T_* = \frac{E}{2R}\left[D - \ln D + \frac{\ln D}{D}\right]^{-1},\quad D = \frac{1}{2}\ln\left(\frac{\lambda\rho Qk_0E}{2Rq^2}\right) \tag{10}$$

In Ref.28, an equation obtained by the method of integral relationships

$$t_* = \frac{c\rho\lambda\ (T_* - T_0)^2}{q^2}[1 + \theta_0^{-1}\ln(2\theta_0)]^2,\quad \theta_0 = \frac{E\ (T_* - T_0)}{RT_*^2} \tag{11}$$

was used; the ignition criterion (6) with $\sigma_0 = 1$ was used to determine T_*.

Table 4 compares the values of t_* for nitrocellulose, calculated by the three methods indicated for different values of q and T_0. The appreciable difference between the results indicates that the approximate methods[28,56] are insufficiently rigorous. The range of existence of non-degenerate ignition conditions for a substance for q = const is given by Eqn.(7) with $n = 0$. Using the relationships which follow from Eqn.(9) for $n = 0$,

$$Z_0 = q^{3/2}t_*^{-1/4}T_*^{-1}\delta_0^{1/2},\quad T_* = T_0 + 2q\,[t_*(\pi\lambda\rho c)^{-1}]^{1/2}$$

Eqn.(8) can be transformed to

$$\ln\left[\frac{(T_* - T_0)^{3/2}}{T_*t_*}\right] = 2\ln[2.78(\pi c)^{-1/2}\cdot(Qk_0)^{1/2}\cdot(R/E)^{1/4}] - \frac{E}{RT_*} \tag{12}$$

and can be used to determine the thermokinetic constants from experimental data. Fig.3 gives the results of experiments on the ignition of "N" powder,[57] which lie on a straight line on the coordinates of Eqn.(12). The use of the thermophysical constants from Ref.42 and Eqn.(12) gives the values $E = 147.8$ kJ mole^{-1}, $Qk_0 = 4.97 \times 10^{20}$ W kg^{-1}.

Although the asymptotic approach developed in Ref.44 does not make it possible to establish the range of existence of non-degenerate ignition conditions, to determine the values of σ_0, T_i, and η_*, or to obtain a universal straight line (12), it nevertheless gives good agreement between the calculated principal characteristics of the ignition of a substance by a constant thermal flux, and the results obtained by numerical integration using a computer. This indicates the advantage of using asymptotic analysis to study the ignition process.

Table 4. Delay time for the ignition of nitrocellulose by a constant thermal flux.

$\lg t_*^0$ [s] for T_0, K			Method of calculation	Refs.
220	300	340		
$q = 10^4$ W m^{-2}				
1.9562	1.8475	1.5781	I	[54]
2.1558	1.8740	1.6892	II	[56]
2.4517	2.2065	2.0499	III	[28]
$q = 10^6$ W m^{-2}				
−2.0438	−2.1525	−2.4219	I	[54]
−1.5545	−1.7467	−1.8616	II	[56]
−1.2509	−1.4178	−1.5158	III	[28]

Note. I—calculation using the asymptotic equations (3)–(5); II—calculation using the interpolation equation (10); III—calculation by the method of integral relationships (Eqn. (11)).

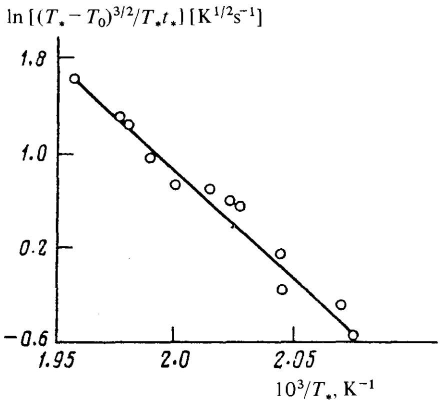

Figure 3. Determination of the thermokinetic constants of "N" powder from experimental data;[57] continuous line—calculation by the least-squares method, points—experiment.

3. The Ignition of Non-transparent Condensed Substances

The simplest case of the ignition of a substance by a stream of hot gas having a constant temperature T_c ($T_c > T_0$) can be considered. In this case, the heat exchange at the surface of the substance ($x = 0$) can be described using Newton's law

$$-\lambda T_x = \alpha\,[T_c - T(0, t)] \tag{13}$$

where α is the coefficient of heat transfer from the gas to the substance (a constant quantity). This problem was previously analysed using the methods of the critical condition,[7,10,18,46,51] breakdown into stages,[24] and integral relationships.[28] These approximate methods do not give sufficient accuracy, however, since they do not use the analytical procedure of the method of compound asymptotic approximations.[40,48,58] As shown below, the latter makes it possible to establish the ignition criterion and the range of existence of non-degenerate ignition conditions, and also to calculate the principal characteristics of ignition and to construct a universal straight line for calculating the kinetic constants from experimental data.

The ignition criterion in this case has a form analogous to that of Eqn.(6)

$$\alpha\,(T_c - T_*) = \sigma\left\{\lambda\rho Q k_0 \frac{RT_*^2}{E}\exp\left(-\frac{E}{RT_*}\right)\right\}^{1/2} \tag{14}$$

where

$$\sigma = \frac{\theta_0^{1/4}}{(0.65)^{1/2}}\left(\frac{T_c - T_*}{T_* - T_0}\right)^{1/4} F^{1/4}(x_0),\quad x_0 = \varphi(y),\quad y = \frac{T_c - T_*}{T_c - T_0},$$

$$F(x_0) = \frac{y(x_0)}{(\pi x_0)^{-1/2} - y(x_0)},\quad y = \exp(x_0)\,\mathrm{erfc}\,[x_0^{1/2}]$$

The value of σ obtained differs considerably from other published values: $\sigma = 1$,[10,51] 4.2,[46] and $(0.1\,\pi\theta_0)^{1/2}$.[7] Eqn.(14) can be used to find the scale temperature T_* and then to calculate the quantity $x_0 = \phi(y)$ and the ignition delay time:

$$t_* = c\rho\lambda\alpha^{-2}x_0 \tag{15}$$

The ignition temperature T_i and the minimum energy of ignition Q_* are calculated using the equations:

$$T_i = T_*\left[1 + 0.5\frac{T_*}{T_0}\,\varepsilon\ln(1/\varepsilon)\right]$$

$$Q_* = c\rho\,(\lambda/\alpha)\,(T_c - T_0)\,[2\,(x_0/\pi)^{1/2} + \exp(x_0)\,\mathrm{erfc}\,[x_0^{1/2}] - 1]$$

Eqns.(14) and (15) can be used to compare the results of the calculation of the ignition delay time t_* by the asymptotic method and by the method used in Refs.10 and 51 (for $\sigma = 1$). Fig.4*a* compares the dependence of t_* on α for nitrocellulose, calculated for T_0 = 303 K, with the experimental data.[59] The relationship has the form $t_* \sim \alpha^{-m}$ noted earlier.[46] Fig.4*b* shows that the function $m = m(T_c)$ obtained by the asymptotic method practically coincides with the curve obtained by numerical integration using a computer and interpolation, with the form:[46]

$$m = 1.79 - 44\left[\frac{RT_0T_c}{E\,(T_c - T_0)}\right]^{1.67} \tag{16}$$

The experimental value $m = 1.64$ for T_c = 573 K[60] also lies satisfactorily on the calculated curve. The curves obtained by the method of Refs.10 and 51 differ considerably from the asymptotic relationships, indicating that the use of the ignition criterion with $\sigma = 1$ is not sufficiently correct.

The asymptotic approach also makes it possible to determine the kinetic parameters E and Qk_0 from experimental data on the ignition of a substance in a stream of hot gas. No accurate relationships for calculating E and Qk_0 have been published, and the method used in Refs.51 and 57, based on the use of the ignition criterion (14) with $\sigma = 1$, as noted above, leads to errors. The method proposed in Ref.60 also is not universal, although it enabled the authors of Ref.59 to carry out the treatment of experimental data on the ignition of a number of substances. The best-justified method for determining the kinetic constants from experimental data is that described in Ref.58. If in the experiment the conditions of heat exchange (T_c, α) are recorded, and the initial temperature of the substance T_0 and the ignition delay time t_* measured, then Eqns.(14) and (15) in the coordinates $\{\ln Z_0,\ 10^3/T_*\}$ can be used to obtain the equation of a universal straight line for determining the kinetic parameters

$$\ln Z_0 = \ln\left[(0.65)^{-1}\lambda\rho Qk_0 (R/E)^{1/2}\right] - \frac{E}{RT_*} \qquad (17)$$

where

$$Z_0 = \alpha^2 T_*^{-1}(T_c - T_*)(T_c - T_0)^{1/2}\left[(\pi x_0)^{-1/2} - y\right]^{1/2},$$
$$T_* = T_c - (T_c - T_0)\exp\left[\frac{\alpha^2 t_*}{c\rho\lambda}\right]\operatorname{erfc}\left[\left(\frac{\alpha^2 t_*}{c\rho\lambda}\right)^{1/2}\right]$$

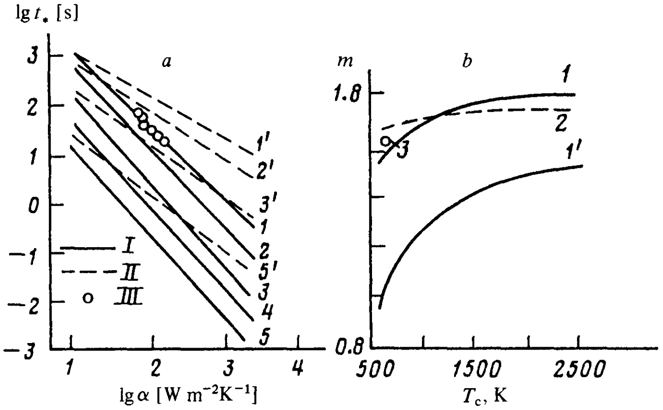

Figure 4. *a*) Dependence of the ignition delay time of nitrocellulose on the thermal properties of the external medium for T_c, K: *1, 1'*) 600; *2, 2'*) 700; *3, 3'*) 1000; *4*) 1800; *5, 5'*) 2500 (*I*—calculation using Eqns.(14) and (15); *II*—calculation by the method of Refs.10 and 51; *III*—experiment[59]); *b*) dependence of the parameter *m* on the temperature T_c: *1*) calculation using Eqns.(14) and (15), *1'*) calculation by the methods of Refs.10 and 51, *2*) calculation using Eqn.(16), *3*) experiment.[60]

As an illustration, *E* and Qk_0 can be calculated for nitrocellulose using published experimental data[60] for $T_0 = 298$ K and $T_c = 573$ K. The least-squares method and treatment of the experimental data on coordinates $\{\ln Z_0,\ 10^3/T_*\}$ gives the linear equation

$$\ln Z_0 = 61.7386 - 24.1843\,\frac{10^3}{T_*}$$

With allowance for Eqn.(17) this gives

$$E = 2.012 \times 10^5 \text{ J mole}^{-1};\quad Qk_0 = 3.475 \times 10^{26} \text{ W kg}^{-1}$$

The value of Qk_0 obtained is 19.5 times that previously calculated by other methods.[10] This is apparently due to the inadequacy of the mathematical model adopted for the calculations, and of the physical experiment,[60] where in addition to convective heat exchange between nitrocellulose and the gas stream, radiant heat exchange from the walls of the vessel also took place. According to the authors' estimates it amounted to ~30% of the total heat exchange.

The asymptotic approach also makes it possible to find the range of existence of non-degenerate ignition conditions

$$\alpha^-(T_0, T_c) \leqslant \alpha \leqslant \alpha^+(T_0, T_c) \qquad (18)$$

The corresponding data are given in Fig.5. The thermophysical and thermokinetic characteristics were taken from Ref.10. It can be seen that with increase in T_0 and decrease in the temperature of the hot gas T_c, the range of existence of non-degenerate ignition conditions becomes much narrower. This important feature must be taken into account when carrying out experiments.

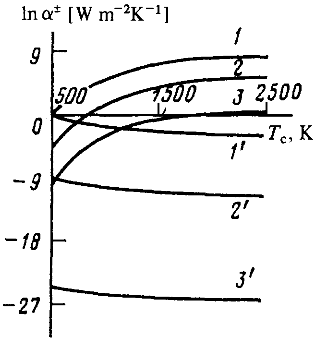

Figure 5. Ranges of existence of non-degnerate ignition conditions for nitrocellulose at T_0, K: *1, 1'*) 383, *2, 2'*) 303; *3, 3'*) 223; α^+—curves *1, 2*, and *3*; α^-—curves *1'*, *2'*, and *3'*.

The approximate equation $t_* \cong C\exp(E/RT_*)$ given in Ref.10, under the conditions of convective heating, makes it possible to calculate with an accuracy reaching 10% only the activation energy from the experimental values of t_*, T_c, α, and T_0, but gives no answer to the question of the magnitude of Qk_0. Calculations carried out by the asymptotic method for octogen, hexogen, nitrocellulose, and "N" powder confirmed this important conclusion and demonstrated again the practical applicability of Eqn.(17).

4. The Ignition of Non-transparent Condensed Substances Using a Heated Block

The simplest thermal model for the ignition of non-volatile condensed systems by a heated block assuming that a zeroth-order reaction takes place has been examined by many workers using various approximate analytical and numerical methods.[8,26–28,44,45,61–65] The lack of agreement between the results obtained, however, indicates that the approximate methods used are insufficiently accurate. Allowance for the combustion of the substance during the ignition delay time was made only in Ref.63, but the equation proposed in this study for calculating the conditional degeneration boundary gives results which are too high.

The present section gives the results of applying the asymptotic theory of the ignition of reacting substances; the examination is carried out for a boundary condition of the first kind without allowance for phase transformations and the large number of kinetic and physical stages, and also without allowance for the dispersal of the substance by the expanding gaseous reaction products. For ideal heat exchange between the substance and the heated block, the system of equations (1) is examined, and the conditions at the surface are written in the form $T(0,t) = T_b$, where T_b is the temperature of the heated block. In Refs.66 and 67, a complete asymptotic analysis of the problem was carried out, and its analytical solution given (in dimensionless units)

$$\left.\tau_* = \frac{\theta_0^2}{2\pi}[1 + 2\theta_0^{-1}\ln\theta_0],\ \tau_i = \frac{\theta_0^2}{2\pi}[1 + 2\theta_0^{-1}\ln\theta_0 + 7.545\theta_0^{-1}]\right\} \quad (19)$$

$$\left.\begin{array}{l}\Delta H = 2^{1/2}\pi^{-1}H_0\theta_0^2[1 + \theta_0^{-1}\ln\theta_0],\ H_0 = c\rho(\varkappa t_0)^{1/2}\cdot(RT_b^2/E),\\ \Delta Q = 2^{-1/2}\pi^{-1}H_0\theta_0^2\{[\theta_0^{-1}(1+\theta_0^{-1})]^{1/2} + 0.5(\arcsin(-1+2\theta_0^{-1}) - 0.5\pi]\},\\ \Delta R = \Delta H - \Delta Q, (\Delta R/H_0) = 0.297 - 0.372 \text{ for } \theta_0 = 10-30,\\ \eta_* = 1 - \exp(-\gamma\tau_*),\ \eta_i = 1 - \exp(-\gamma\tau_i)\end{array}\right\} \quad (20)$$

where

$$\tau = t/t_0,\ t_0 = \frac{cRT_b^2}{EQk_0}\exp\left(\frac{E}{RT_b}\right),\ \gamma = \frac{cRT_b^2}{QE} \quad (21)$$

Here, t is the current time, t_0 the adiabatic induction period of the thermal explosion at T_b, τ_* the dimensionless warm-up time of the specimen, τ_i the dimensionless ignition delay time, θ_0 the temperature head of the heating block ($\theta_0 \gg 1$), η_* the depth of combustion in the warm-up time, η_i the depth of combustion in the ignition delay time, and ΔH, ΔQ, and ΔR the stored energy, the energy supplied from outside, and the energy liberated in the reaction respectively.

Eqns.(19) and (20) were obtained neglecting the quantity $\beta = RT_b/E$ and with the condition that the warm-up of the substance is complete at the moment t_* when the temperature gradient at the surface becomes zero, and the ignition of the substance takes place at the moment t_i when the temperature gradient at the surface becomes infinite. For sufficiently small values of $\gamma\theta_0^2$, the equations for η_* and η_i are simplified and take the form

$$\eta_* = \gamma\tau_*,\ \eta_i = \gamma\tau_i \quad (22)$$

The conditional boundary of degeneration of normal ignition conditions can be determined from the inequalities $\eta_* \leqslant a$, $\eta_i \leq a$, where $a = 0.1-0.2$.[66] Eqn.(20) is then used to find the equation for calculating the limiting value of the parameter γ characterising the conditional boundary of degeneration

$$\gamma \leqslant \gamma_0 = \tau_i^{-1}\cdot\ln[1/(1-a)] \quad (23)$$

The equation proposed in Ref.63 has the form $\gamma_0 = 0.5\,\theta_0^{-1}$ and gives results which are 1–2 times higher than those given by Eqn.(23).

The accuracy of the asymptotic equations for calculating the basic characteristics of ignition is extremely high, as indicated by comparing with the results of numerical integration using a computer (Table 5). Fig.6 compares the results of the calculation of the warm-up periods of a reacting substance τ_* for $\beta = 0$ with the approximate equations used by a number of authors and also with Eqn.(19). The results of the calculation using Eqn.(19) practically coincide with those obtained[61] by computer calculation. Curves *2* and *3*, calculated using the data of Refs.27 and 63, are close to one another. The results obtained in Ref.26 (curve *1*) and in Ref.64 (curve *7*) are extremely far from the true values of the warm-up period. Most authors have tried to obtain simplified equations for calculating the warm-up time in the form of functions $\tau_* = A\theta_0^2$; the coefficient A has been assigned the values 0.21,[68] 0.207,[65] 0.25,[27,28] and 0.159.[45,62] This simplification, however, leads to marked deviations from the results obtained using Eqn.(19).

The asymptotic method has been used[44] to obtain more rigorous values of τ_*. Although the authors[44] did not use this method in complete form to solve the problem of the ignition of a substance by a heated block, they were able to estimate the lower and upper values of τ_* (denoted τ_*^- and τ_*^+ respectively). Table 6 gives the values of τ_*^- and τ_*^+ from Ref.44, and also compares the values of τ_* calculated using Eqn.(19) and obtained by numerical integration using a computer.[61] Good quantitative agreement is observed. As $\theta_0 \to \infty$, Eqns.(19) are simplified, and in the limit give the values obtained in Refs.45 and 62. This limit, however, is only the zeroth asymptotic approximation to the actual value of the warm-up period of the substance; this approximation does not give the required accuracy.

Table 5. Dimensionless characteristics of the ignition of a condensed substance by a heated block.

Ignition characteristic	θ_0					Method of calculation	Refs.
	10	15	20	25	30		
τ_*	25.7	51.6	86.2	129.5	181.5	I	[61]
	23.2	48.7	82.7	125.1	175.7	II	[66, 67]
τ_i	37.3	67.7	106.2	152.9	207.7	I	[61]
	35.2	66.7	106.7	155.1	211.7	II	[66, 67]
$\Delta Q/H_0$	40.0	84.75	146.0	223.8	318.0	I	[61]
	35.5	79.7	141.4	220.8	315.8	II	[66, 67]

Note. I—numerical integration using a computer; II—calculation using the asymptotic equations (19) and (20).

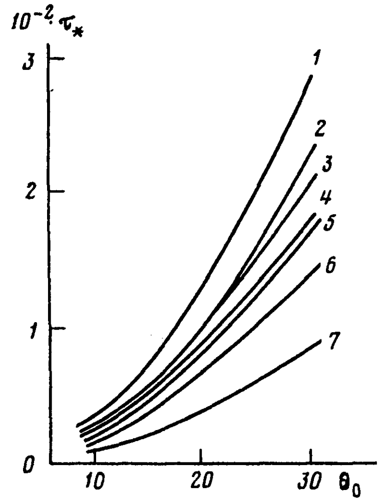

Figure 6. Dependence of the dimensionless warm-up time of a reacting substance τ_* on the parameter θ_0, calculated from various data: *1*) Ref.26, *2*) Ref.27, *3*) Ref.63, *4*) Ref.61, *5*) from Eqn.(19), *6*) Ref.45, *7*) Ref.64.

Fig.7 gives the results of the calculation, using Eqns.(20) and (22) for η_*, of the boundary conditions of the degeneration of the normal ignition conditions of nitrocellulose. Nondegenerate ignition conditions are produced at temperatures lying below the corresponding curves *1–3*, each of which corresponds to a definite value of the parameter a. Using Eqn.(21), Eqns.(19) can be represented in a form convenient for determining the kinetic constants, that is they can be linearised. For example, the following expression is obtained for the warm-up time

$$\ln\left[\frac{t_*}{T_b-T_0}\right]=\frac{E}{RT_b}+\ln\left\{\frac{c}{2\pi Qk_0}\left[\frac{E(T_b-T_0)}{RT_b^2}+2\ln\left(\frac{E(T_b-T_0)}{RT_b^2}\right)\right]\right\} \tag{24}$$

Table 6. Comparison of ignition delay times calculated by different methods.

Ignition characteristic	θ_0			Method of calculation	Refs.
	10	20	30		
τ_*	25.7	86.2	181.5	I	[61]
τ_*	23.2	82.7	175.7	II	[66, 67]
τ_*^-	20.9	74.6	160.7	III	[44]
τ_*^+	28.7	97.4	203.3	III	[44]

Note: I—numerical integration using a computer; II—calculation using the asymptotic equation (19); III—calculation by the asymptotic method.

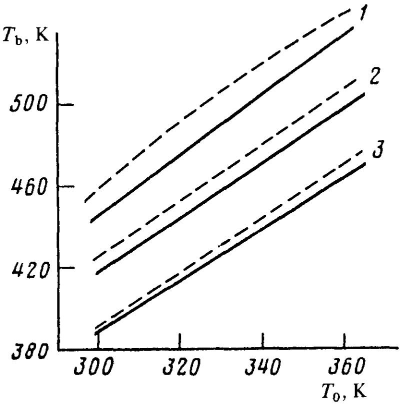

Figure 7. Conditional boundaries of the degeneration of the normal ignition conditions of nitrocellulose for values of the parameter a: 1) 0.2; 2) 0.15; 3) 0.1; continuous lines—calculation using Eqn.(20), broken line—calculation using Eqn.(22).

The results of an experimental study of the ignition of nitrocellulose by a heated block with a temperature T_b = 485–515 K at a temperature of the specimens T_0 = 293–298 K have been published.[69] Fig.8 gives these results, treated by the least-squares method on the coordinates of Eqn.(24). In the treatment of the experimental data, allowance was made for the fact that under the conditions of the experiment, the quantity $(T_b-T_0)/T_b^2$ varied within a range of 5%. Assuming that the average value of this quantity is 0.816×10^{-3} K^{-1}, treatment of the experimental data[69] using Eqn.(24) gives E = 200 kJ mole^{-1} and $Qk_0 = 1.08 \times 10^{26}$ W kg^{-1}. Treatment of the data of the same experiment using the equation for the delay time τ_i gives the value $Qk_0 = 7.45 \times 10^{26}$ W kg^{-1}.

Thus the ignition criterion in the problem with boundary conditions of the first kind is the "explosion" of the temperature gradient on the surface of the substance at the moment of ignition, whereas in problems with boundary conditions of the second and third kind the criterion is the "explosion" of the actual temperature at the surface of the substance.

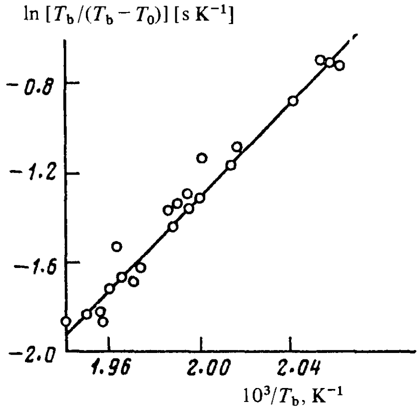

Figure 8. Determination of the thermokinetic parameters of the ignition of nitrocellulose from experimental data:[69] continuous line—calculation by the least-squares method, points—experiment.

5. The Ignition of a Semi-transparent Substance by a Beam of Radiant Energy

In the last ten years, studies of the combustibility of condensed systems using a CO_2 laser (wavelength 10.6 μm) have found extensive application in various branches of science and technology. They make it possible to carry out experiments at appreciable thermal flux densities and to take correct account of the bulk character of the absorption of light by the substance. The problem of the ignition of a semi-transparent substance by a beam of radiant energy has been studied by numerical and approximate analytical methods by many authors.[10,18,21,24,39,42,44,56,70,71] The works cited, however, give no single expression for the ignition criterion, do not indicate the ranges of existence of non-degenerate ignition conditions, and do not contain universal linear equations making it possible to solve the inverse problem of calculating the thermokinetic parameters from experimental data on the ignition of a substance by a beam of radiant energy.

The mathematical formulation of the problem with the notation given above has the form:[72]

$$\begin{gathered}T_t=\varkappa T_{xx}+Qk_0c^{-1}(1-\eta)\exp(-E/RT)+q\nu(c\rho)^{-1}\exp(-\nu x),\\ \eta_t=k_0(1-\eta)\exp(-E/RT);\ t=0:\ T=T_0,\ \eta=0;\\ x=0:\ T_x=0;\ x=\infty:\ T=T_0\end{gathered} \tag{25}$$

Here, q is the density of the beam of radiant energy, and ν the coefficient of bulk absorption of energy at a given wavelength.

The principal results obtained using the asymptotic theory of ignition described in Refs.72 and 73 will be given. The parameter $\nu_1 = \nu\lambda T_0 q^{-1}$ is introduced, representing the ratio of the thickness of the heated layer to the thickness of the absorption zone. In the case where $\nu_1 \gg 1$, the ignition criterion has a form analogous to that of Eqn.(6):

$$q=\sigma\left\{\lambda\rho Qk_0\frac{RT_*^2}{E}\exp\left(-\frac{E}{RT_*}\right)\right\}^{1/2},\ \sigma=\left[\frac{\Phi(\alpha)}{0.65}\right]^{1/2}\theta_0^{1/4}\left[(\theta_*-1)\frac{d\theta_*}{du_*}\right]^{-1/4} \quad (26)$$

where

$$\alpha=\nu_1\varepsilon\theta_*^2,\ \Phi(\alpha)=(\alpha)^{1/\alpha-1}\cdot\gamma\left(\frac{1}{\alpha},\frac{1}{\alpha}\right)\exp\left(\frac{1}{\alpha}\right),$$
$$\theta_*=1+2(u_*/\pi)^{1/2}-\frac{1}{\nu_1}+\frac{1}{\nu_1}\exp(\nu_1^2u_*)\,\mathrm{erfc}\,[(\nu_1^2u_*)^{1/2}], \quad (27)$$
$$\gamma(n,m)=\int_0^m t^{n-1}\exp(-t)\,dt$$

Eqn.(26), with allowance for Eqn.(27), can be used to calculate the dimensionless ignition delay time u_*, and hence the values of θ_* and $d\theta_*/du_*$. The dimensional characteristics of the ignition are calculated from the equations

$$t_*=\left(\frac{\lambda T_0}{q}\right)^2\frac{u_*}{\varkappa},\ T_*=T_0\theta_*,\ T_\mathrm{i}=T_*[1+0.5\theta_*\varepsilon\ln(1/\varepsilon)],$$
$$\eta_*=1.48\gamma\varepsilon^{-1/2}\cdot\theta_*\left(\frac{d\theta_*}{du_*}\right)^{-1/2}\cdot[\Phi(\alpha)]^{-1} \quad (28)$$

As $\nu_1\to\infty$, Eqns.(26) and (27) lead to the familiar result given in the section on the ignition of a non-transparent substance: $\sigma_0 = 1.39\,\theta_0^{1/4}$.

Eqn.(26) and the function θ_* are readily transformed to

$$\ln Z_0=\ln\left[\frac{\rho Qk_0}{0.65}\left(\frac{R\lambda}{E}\right)^{1/2}\right]-\frac{E}{RT_*} \quad (29)$$

$$Z_0=\frac{q^{3/2}[\nu y(t_*)]^{1/2}}{T_*\Phi(\alpha)},\ T_*=T_0+\frac{q}{\nu\lambda}\left[y(t_*)+2\left(\frac{\varkappa\nu^2t_*}{\pi}\right)^{1/2}-1\right],$$
$$y(t_*)=\exp[\varkappa\nu^2t_*]\,\mathrm{erfc}\,[(\varkappa\nu^2t_*)^{1/2}] \quad (30)$$

If the quantities T_0, q, ν, and t_* are measured experimentally Eqn.(30) can be used to calculate T_*, y, and Z_0, and, having expressed the experimentally obtained relationships on coordinates $\{\ln Z_0,\ 10^3/T_*\}$, Eqn.(29) can be used to calculate the thermokinetic constants E and Qk_0. The ignition characteristics of nitrocellulose t_* and T_* calculated from Eqns.(28) for T_0 = 293 K show good quantitative agreement with the same quantities obtained by the method used in Refs.10, 21, and 56.

For the case where $\nu_1 = 0$ (1), when the thicknesses of the heated layer and the absorption zone are commensurate, the function σ in the expression for the ignition criterion (26) has the form:

$$\sigma=\theta_0^{1/2}\left[(\theta_*-1)\frac{d\theta_*}{du_*}\right]^{-1/2}\exp\left[-\frac{C}{2}\bar{x}^m\right] \quad (31)$$

where

$$\bar{x}=\nu_1^2u_*=\varkappa\nu^2t_* \quad (32)$$

and the values of the constants C and m are given in Ref.72.

Eqn.(26) can be used to calculate the dimensionless delay time $\bar{x}$, and hence θ_* and $d\theta_*/du_*$ from Eqns.(27) and t_* from Eqn.(32). The temperatures T_* and T_i are then determined:

$$T_*=T_0\theta_*,\ T_\mathrm{i}=T_*[1+0.75\,\theta_*\varepsilon\ln(1/\varepsilon)] \quad (33)$$

Eqn.(26), in which σ is given by Eqn.(31), can also be represented in the form of the universal linear equation:

$$\ln[\nu q\exp(C\bar{x}^m+\bar{x})\,\mathrm{erfc}\,(\bar{x}^{1/2})]=\ln(\rho Qk_0)-\frac{E}{RT_*} \quad (34)$$

The value of T_* is calculated from the experimental values of $\{T_0,\ q,\ \nu,\ t_*\}$ using Eqn.(30), and the left-hand side of Eqn.(34) is calculated from the value of $\bar{x}$ using Eqn.(32). By treating the experimental results by the least-squares method and using Eqn.(34) it is possible to calculate E and Qk_0. Fig.9 gives experimental data[56] on the ignition of nitrocellulose ($\nu = 3\times10^4$ m^{-1}) and nitrocellulose containing 1% carbon ($\nu = 6\times10^4$ m^{-1}) for T_0 = 293 K. Treatment of these data on coordinates $\{\ln Z_0,\ 10^3/T_*\}$, where $\ln Z_0$ is the left-hand side of Eqn.(34), makes it possible to calculate the thermokinetic parameters

$$E = 192767\ \text{J mole}^{-1},\ Qk_0 = 2.1\times10^{25}\ \text{W kg}^{-1}$$

in good agreement with the values given in Ref.10.

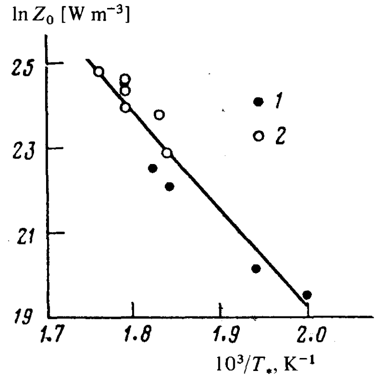

Figure 9. Determination of the thermokinetic constants of the ignition of nitrocellulose from experimental data;[56] continuous line—calculation by the least-squares method; *1, 2*) experimental points obtained for the following values of ν, m^{-1}: *1*) 3×10^4, *2*) 6×10^4.

Comparison of the results of the calculation of the ignition characteristics t_* and T_* by the asymptotic method (31)–(33) with the results in Refs.10, 21, and 56 on the whole shows good quantitative agreement and, which is particularly important, indicates that the "asymptotic" values practically coincide with the values obtained by numerical integration using a computer.[21] An exception is the method of Ref.56, where in the estimation of the scale temperature T_* no account is taken of the change in the value of ν, so that the values obtained are too high.

If the thickness of the heated layer is much less than the thickness of the absorption zone, that is for $\nu_1 \ll 1$, the absorption of energy in the zone of the chemical reaction is slight, and the substance heats up slowly. In this case the ignition process becomes degenerate and resembles the conditions of thermal explosion. The principal characteristics of ignition can be calculated using the equations

$$T_*=\frac{E}{R}\left[\ln\left(\frac{\rho Qk_0}{q\nu}\right)\right]^{-1},\quad t_*=\frac{c\rho}{\nu q}(T_*-T_0),\ \theta_*=\frac{T_*}{T_0},$$
$$T_\mathrm{i}=T_*[1+\theta_*\varepsilon\ln(1/\varepsilon)],\ \eta_*=\gamma\theta_*^2\ln(1/\varepsilon) \quad (35)$$

with the condition that

$$q>q_m=\rho Qk_0\nu^{-1}\exp(-E/RT_0)$$

Eqn.(35) readily gives the universal straight-line equation

$$\ln(q\nu/\rho)=\ln(Qk_0)-E/RT_*,\ T_*=T_0+\nu qt_*/c\rho \quad (36)$$

which makes it possible to treat experimental data in the range $\nu_1 \ll 1$ and to calculate the thermokinetic parameters for the values of T_0, q, ν, and t_* recorded in the experiment. Comparison of the results of the calculations using

Eqns.(35) and the methods of Refs.10, 21, and 56 shows that none of these methods gives satisfactory results in the range of variation in the parameter ν_1 examined. This is revealed by the excessively high value of T_*[10,21] and by the fact that T_* is completely insensitive to change in ν.[56] Only the asymptotic method[35] gives acceptable results in the range $0.009 \leq \nu_1 \leq 0.1$, confirming again the usefulness of its practical application.

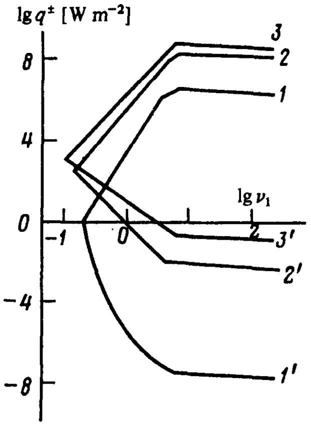

Figure 10. Ranges of existence of non-degenerate conditions for the ignition of nitrocellulose by laser radiation for T_0, K: *1, 1'*) 223; *2, 2'*) 293; *3, 3'*) 323; curves *1*–*3* correspond to q^+, and curves *1'*–*3'* correspond to q^-.

Fig.10 gives the ranges of existence of non-degenerate ignition conditions for nitrocellulose, calculated with allowance for the thermophysical and thermokinetic constants from Ref.10, for three values of the initial temperature T_0 for the cases $\nu_1 = 0$ (1) and $\nu_1 \gg 1$, when the thickness of the heated layer is much greater than or commensurate with the thickness of the absorption zone.[73] The ignition conditions are non-degenerate if the following condition is satisfied:

$$q^-(T_0, \nu_1) \leqslant q \leqslant q^+(T_0, \nu_1) \tag{37}$$

For $q \gg q^+$, the thickness of the heated layer is small, and "superficial burning" of the substance is observed, and for $q \ll q^-$, the thickness of the heated layer is appreciable and ignition does not take place. In neither case does the ignition process take place in two stages, since the warm-up of the substance is accompanied by spontaneous chemical heating with an appreciable energy contribution from the chemical reaction.

III. THE IGNITION OF NON-TRANSPARENT CONDENSED SYSTEMS ON THE PULSED INTRODUCTION OF HEAT, WITH HEAT LOSSES, AND ON UNSYMMETRICAL HEATING

1. Pulse Ignition Conditions

The development of a self-accelerating reaction in a reacting substance and the formation of a sufficiently wide heated layer requires the definite action of an external energy source on the substance. If the external source acts for a limited time, then under certain conditions, ignition of the substance may not take place. Pulse ignition conditions have been studied[7,9,10,17,43,68,74] by numerical and analytical methods using the Zel'dovich criterion,[3] applicable only to the problem of the unsymmetrical ignition of a thin slab of substance by a heated block. The aim of the works cited was to determine the critical ignition conditions. A more general problem, however, is the determination of the ranges of existence of non-degenerate ignition conditions, examined above for the problems of the thermal theory, in which the continuous supply of heat from the source is assumed.

The problem of the ignition of a substance with stepwise change in the density of the thermal flux at its surface ($x = 0$) is examined below:

$$-\lambda T_x = \begin{cases} q_1, & 0 < t < t_0 \\ q_2, & t > t_0 \end{cases} \qquad q_1 > q_2 > 0 \tag{38}$$

This problem has been studied[75] by the method of compound asymptotic expansions[48] without introducing any of the additional conditions used in Refs.10 and 74. The ignition criterion for the pulsed introduction of heat is given by the expression:

$$q_1 q_2 = 1.5385\varepsilon^{1/2} Q\rho k_0 \lambda T_0 \theta_* \left(\frac{d\theta_*}{du_*}\right)^{-1/2} \exp(-1/\varepsilon\theta_*) \tag{39}$$

where

$$\theta_* = 1 = 2\pi^{-1/2}[u_*^{1/2} - A_0(u_* - u_0)^{1/2}],\ A_0 = 1 - q_2/q_1,\ u_0 = \varkappa t_0(\lambda T_0/q_1)^{-2},$$
$$u_* = \varkappa t_*(\lambda T_0/q_1)^{-2},\ u_* > u_0 \tag{40}$$

The calculation of the dimensionless quantity u_* and hence the calculation of the quantities θ_* and $d\theta_*/du_*$ is carried out using Eqn.(39), and the dimensional characteristics of the ignition are calculated using the equations

$$t_* = \frac{u_*}{\varkappa}\left(\frac{\lambda T_0}{q_1}\right)^2,\ T_* = T_0\theta_*,\ T_i = T_*[1 + 0.5\theta_*\varepsilon \ln(1/\varepsilon)],$$

$$\eta_* = 1.48\gamma\varepsilon^{-1/2}\frac{q_2}{q_1}\theta_*\left(\frac{d\theta_*}{du_*}\right)^{-1/2},\quad Q_* = \frac{c\rho\lambda T_0^2}{q_1}\left[u_0 + \frac{q_2}{q_1}(u_* - u_0)\right] \tag{41}$$

In the limiting particular case $A_0 = 0$, $q_2 = q_1$, Eqns.(39)–(41) can be used to calculate all the characteristics of ignition for the continuous action of a source with a flux density q_1.

Eqn.(39) can be represented on coordinates $\{\ln Z_0, 10^3/T_*\}$ in the form of the universal straight-line equation

$$\ln Z_0 = \ln\{1.5385 Q\rho k_0 (\pi\varkappa)^{1/4}(R\lambda/E)^{1/2}\} - \frac{E}{RT_*} \tag{42}$$

where

$$Z_0 = \frac{q_1^{1/2} q_2 [(t_* - t_0)^{1/2} - A_0 t_*^{1/2}]^{1/2}}{T_*[t_*(t_* - t_0)]^{1/4}},\ T_* = T_0 + \frac{2q_1[t_*^{1/2} - A_0(t_* - t_0)^{1/2}]}{(\pi c\rho\lambda)^{1/2}} \tag{43}$$

If the quantities T_0, t_0, t_*, q_1, q_2 are recorded experimentally, it is possible using the least-squares method in the coordinates indicated to carry out the treatment of the experimental data and to calculate the parameters E and Qk_0. In the particular case $A_0 = 0$, $q_2 = q_1$, Eqns.(43) become

$$Z_0 = q_1^{3/2} T_*^{-1} t_*^{-1/4},\quad T_* = T_0 + 2q_1(t_*/\pi c\rho\lambda)^{1/2}$$

The range of existence of non-degenerate pulse ignition conditions is given by the inequalities[75]

$$t_0^-(q_1, q_2, T_0) < t_0 < t_0^+(q_1, q_2, T_0) \tag{44}$$

and the switch-over time t_0 is shorter than the ignition delay time $t_*(q_1)$ with continuous action of a source with an energy flux density q_1. Fig.11 illustrates the change in the ranges of the non-degenerate ignition conditions of nitrocellulose for $T = 300$ K in the range of values $q_1 = 10^4$–5×10^6 W m^{-2}, $A_0 = 0.1$–0.9 [75] (the values of the constants from Ref.10 were used).

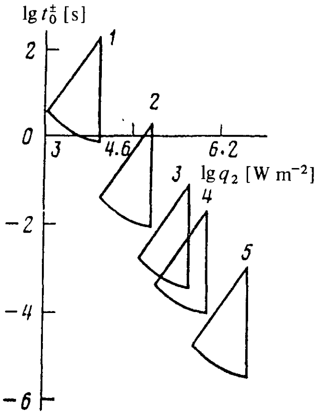

Figure 11. Ranges of existence of non-degenerate conditions for the pulse ignition of nitrocellulose for q_1, W m^{-2}: *1*) 10^4, *2*) 10^5, *3*) 5×10^5, *4*) 10^6, *5*) 5×10^6.

Analysis of the results of the calculation using Eqns.(39)–(41) shows that with decrease in the values of q_2 and t_0 from the range of existence of non-degenerate ignition conditions at a fixed value of the thermal flux density, the ignition delay time increases sharply. This corresponds to the physical picture of pulse ignition conditions.

2. The Ignition of Condensed Systems with Heat Loss from the Lateral Surface of the Specimen

The critical conditions for the ignition of non-transparent condensed substances have been studied by the thermal explosion and integral relationships methods, and approximate equations have been obtained for calculating the ignition delay time for a cylindrical specimen with heat loss from the lateral surface and boundary conditions of the second kind at the ends.[28,56,76] As shown below, however, the methods used[28,56,76] do not ensure sufficient accuracy of the determination of the ignition delay time, do not make it possible to formulate rigorously the ignition criterion, and leave open the questions of the range of existence of non-degenerate ignition conditions and the conversion of the experimental curves to straight lines in a special system of coordinates.

To solve these problems of the thermal theory of ignition, it is possible to examine the "two-dimensional" problem of the ignition of a semi-infinite cylindrical specimen of radius r_0 with heat loss into the surrounding medium, given by Newton's law

$$T_t = \varkappa\,[T_{xx} + r^{-1}(rT_r)_r^{\bullet}] + Qk_0c^{-1}(1-\eta)\exp(-E/RT),$$
$$\eta_t = k_0(1-\eta)\exp(-E/RT);\ t=0:\ T=T_0,\ \eta=0;$$
$$x=\infty:\ T=T_0;\ x=0:\ -\lambda T_x = q;\ r=r_0:\ -\lambda T_r = \alpha(T-T_0) \quad (45)$$

Here, x and r are the longitudinal and radial coordinates respectively, and α the coefficient of heat transfer (a constant quantity) from the lateral surface of the specimen to a surrounding medium with temperature T_0. The problem (45) was solved by averaging[77] with respect to the variable r, and the similarity criterion σ_α determined[78]

$$\sigma_\alpha = \beta\mu_0(\mathrm{Bi}),\ \beta = (\lambda T_0/qr_0)^2,\ \mathrm{Bi} = \alpha r_0/\lambda \quad (46)$$

where $\mu_0(\mathrm{Bi})$ is the function of the Biot criterion, defined and tabulated by Lykov.[79] The ignition criterion according to Ref.78 has the form

$$q = \{1.5385\varepsilon^{1/2}\rho Qk_0\lambda T_0\theta_*(\mathrm{d}\theta_*/\mathrm{d}u_*)^{-1/2}\exp(-1/\varepsilon\theta_*)\}^{1/2} \quad (47)$$

where

$$\theta_* = 1 + (\sigma_\alpha)^{-1/2}\operatorname{erf}[\tilde{x}^{1/2}],\ \frac{\mathrm{d}\theta_*}{\mathrm{d}u_*} = \left(\frac{\sigma_\alpha}{\pi\tilde{x}}\right)^{1/2}\exp(-\tilde{x}) \quad (48)$$

Solving Eqn.(47) gives the dimensionless ignition delay time $\tilde{x}$, and hence the quantities of Eqn.(48) at the moment of ignition. The dimensional characteristics of the ignition of the substance are calculated from the equations

$$T_* = T_0\theta_*,\ T_\mathrm{i} = T_*[1 + 0.5\theta_*\varepsilon\ln(1/\varepsilon)],\ t_* = \frac{\tilde{x}}{\varkappa\sigma_\alpha}\left(\frac{\lambda T_0}{q}\right)^2,$$
$$\eta_* = 1.48\gamma\varepsilon^{-1/2}\theta_*\left(\frac{\mathrm{d}\theta_*}{\mathrm{d}u_*}\right)^{-1/2},\ Q_* = qt_* \quad (49)$$

Eqn.(47) can also be written in the form

$$\ln Z_0 = \ln\left[\frac{\rho Qk_0}{0.65}\left(\frac{R\lambda}{E}\right)^{1/2}(\pi\varkappa)^{1/4}\right] - \frac{E}{RT_*} \quad (50)$$

where

$$\tilde{x} = \varkappa t_* r_0^{-2}\mu_0(\mathrm{Bi}),\ Z_0 = q^{1/2}(T_*t_*^{1/4})^{-1}\exp(-x/2),$$
$$T_* = T_0 + qr_0[\lambda\mu_0^{1/2}(\mathrm{Bi})]^{-1}\operatorname{erf}[\tilde{x}^{1/2}] \quad (51)$$

For $\alpha = 0$, the particular case of ignition without heat loss, examined in section II, is obtained. If the values of T_0, q, α, t_*, and r_0 are recorded experimentally, Eqns.(51) can be used to calculate the values of $\tilde{x}$, T_*, and Z_0, and the least squares method in the coordinates $\{\ln Z_0,\ 10^3/T_*\}$ can be used to determine the coefficients of the linear equation (50), and then the thermokinetic parameters E and Qk_0.

The range of existence of non-degenerate ignition conditions is given by the inequalities[52]

$$\theta_*\left(\frac{\mathrm{d}\theta_*}{\mathrm{d}u_*}\right)^{-1/2} \leqslant \frac{1}{3}\varepsilon^{-1/2},\quad \theta_*\left(\frac{\mathrm{d}\theta_*}{\mathrm{d}u_*}\right)^{1/2} \leqslant \frac{1}{3}\varepsilon^{-1/2}$$

Introducing the ignition criterion (47) gives:[78]

$$q^-(T_0,\sigma_\alpha) \leqslant q \leqslant q^+(T_0,\sigma_\alpha) \quad (52)$$

The ranges of existence of the non-degenerate conditions (52) for the ignition of nitrocellulose are given in Fig.12, and Fig.13 makes it possible to compare the results of the calculation of the ignition delay time t_* from Eqns.(47)–(49) and by the methods of Refs.28 and 76 for $T_0 = 300$ K, $q = 10^4$ W m^{-2}, and $0 < \sigma_\alpha < 2$.

The delay time with heat loss can be calculated using the equation[76]

$$t_* = t_*^0[1 - 1.78t_*^0/d]^{-1},\ d = c\rho\lambda T_0^2/q^2\sigma_\alpha \quad (53)$$

where t_*^0 (without allowance for heat loss) is given by Eqns.(10). In Ref.28 the time t_* was calculated from the equation

$$t_* = d\ln[(1 - t_*^0/d)(1 - 2t_*^0/d)^{-1}] \quad (54)$$

and t_*^0 was determined from Eqns.(11). Fig.13 shows that the methods of Refs.28 and 76 give an unjustifiably high value for the ignition delay time, compared with the asymptotic method (47)–(49). This is due to the insufficient accuracy of the determination of the quantity t_*^0 (see Table 4) and the critical conditions for ignition of the substance.

The problem (45) is readily generalised to the case where there is additional heat loss due to flow over the surface being ignited in the case of conductive and convective heat exchange mechanisms.

Thus the rigorous asymptotic approach also has an appreciable advantage over published approximate methods in the analysis of the ignition of substances with heat loss.

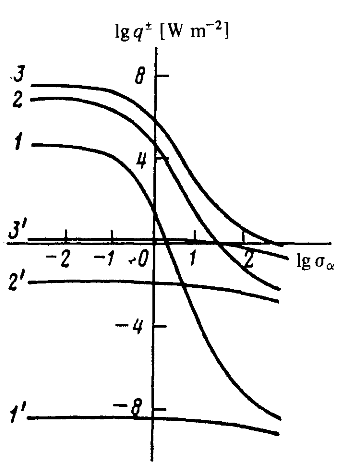

Figure 12. Ranges of existence of non-degenerate conditions for the ignition of nitrocellulose with heat loss for T_0, K: *1,1'*) 220; *2,2'*) 300; *3,3'*) 340; curves *1–3* and *1'–3'* correspond to q^+ and q^- respectively.

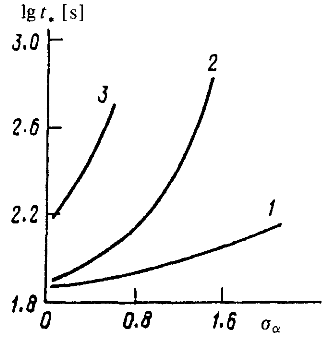

Figure 13. Calculated dependence of the ignition delay time of nitrocellulose on the parameter σ_α: *1*) calculation using Eqn.(49), *2*) calculation using the method of Ref.76, *3*) calculation using the method of Ref.28.

3. The Ignition of Substances with Unsymmetrical Heating

The theory of the ignition of a thin slab of condensed substance with thickness h, for which a constant high temperature T_1 is continuously maintained at one surface, and a low temperature T_2 at the other, has been examined.[3,61,80–82] In Refs.3 and 80, a stationary theory of ignition was developed, and an equation obtained for calculating the heat removed from the reaction zone under critical conditions. It was shown that if the heat removed is lower than a critical value, the slab ignites; otherwise, stationary heat liberation conditions are established. In Ref.61, numerical integration using a computer was used to study the dependence of the warm-up time and the ignition delay time on the parameters of the problem, and also the critical conditions of ignition. In Ref.82, the zeroth approximation of the asymptotic method was used to determine the warm-up time of a substance and to find the critical conditions for ignition. An asymptotic non-stationary theory of unsymmetrical ignition of a substance was developed in Ref.83, where the method of compound expansions was used to obtain equations for calculating the ignition delay time and the energy supplied to and stored by the substance in the warm-up period, and the critical conditions for ignition were found.

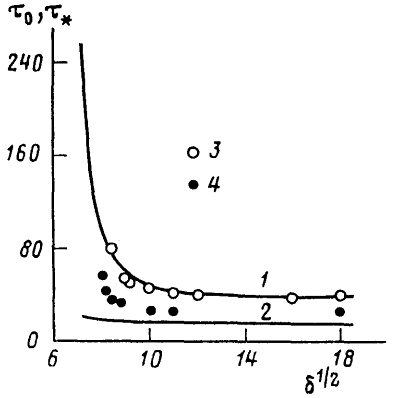

Figure 14. Calculated dependence of the dimensionless ignition delay time τ_* and the warm-up time τ_0 of a reacting substance on $\delta^{1/2}$ for unsymmetrical heating: *1*) τ_* calculated from Eqn.(55), *2*) τ_0 calculated by the method of Ref. 82; the open and black circles give the values of τ_* and τ_0 respectively, obtained by numerical integration.[61]

Fig.14 for $\varepsilon_0 = 0.1$ compares the results of the calculation of the dimensionless ignition delay time τ_* obtained in Refs. 61 and 82 with the results from Ref.83:

$$\tau_* = \delta \sum_{k=0}^{5} \varepsilon_0^{k/4} u_k(\mu), \quad \mu = \varepsilon_0 \delta^{1/4}, \quad u_1 \equiv 0,$$
$$\varepsilon_0 = \frac{RT_1^2}{E(T_1 - T_2)}, \qquad \delta = \frac{E}{RT_1^2} \frac{\rho Q k_0 h^2}{\lambda} \exp(-E/RT_1) \tag{55}$$

Curve *1*, calculated using Eqn.(55), shows good agreement with the results of the numerical integration.[61] At the same time, the values of τ_0, which were also found by numerical integration,[61] do not lie on curve *2*, obtained by the method of Ref.82. Non-degenerate ignition conditions are produced if the following condition is satisfied:[3,61,80,82,83]

$$h > h_* = \left[\frac{E}{2R}\left(\frac{T_1 - T_2}{T_1}\right)^2 \frac{\lambda}{\rho Q k_0} \exp\left(\frac{E}{RT_1}\right)\right]^{1/2} \tag{56}$$

which with allowance for stationary heat removal from the reaction zone gives the critical value of the density of the thermal flux

$$q_* = 2^{1/2}\left[\lambda \rho Q k_0 \frac{RT_1^2}{E} \exp\left(-\frac{E}{RT_1}\right)\right]^{1/2} \tag{57}$$

In the stationary case for $q < q_*$ the slab ignites, and when $q \geqq q_*$, ignition does not take place.

The coefficient $\sigma_0 = 2^{1/2}$ from Eqn.(57) has been used[43] find a criterion for the ignition of a semi-infinite slab by constant thermal flux. This approximation is not rigorous, noted above (section II).

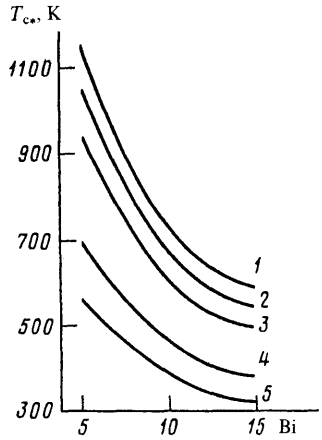

Figure 15. Ranges of existence of non-degenerate conditions for the ignition of spherical nitrocellulose particles in a stream of hot gas for T_0, K: *1*) 340, *2*) 320, *3*) 300, *4*) 250, *5*) 220.

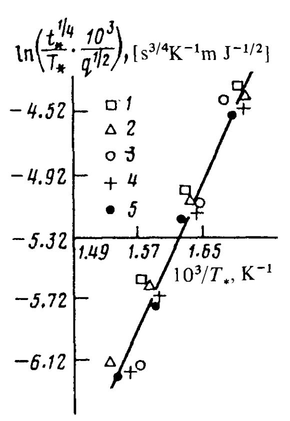

Figure 16. Determination of the thermokinetic constants for the ignition of a composite fuel from experimental data;[32] continuous straight line—calculation by the least-squares method;[87] the experimental points were obtained for T_0, K: *1*) 213, *2*) 243, *3*) 273, *4*) 303, *5*) 333.

V. THE IGNITION OF NON-TRANSPARENT SUBSTANCES N SYMMETRICAL HEATING, AND WHEN HETEROGENEOUS EACTIONS AND MULTI-STAGE CHEMICAL REACTIONS AKE PLACE

The asymptotic method of compound expansions makes it ossible to solve the important applied problem of the igni- on of lamellar, cylindrical, and spherical specimens of a substance in a stream of hot gas, to establish the ignition criterion and the range of existence of non-degenerate conditions, and to construct a universal straight line in a special system of coordinates.[84,85] Fig.15 gives the dependence of the critical temperature of the medium T_{c*} on the Biot criterion and the initial temperature of the substance T_0 for spherical particles of nitrocellulose. Ignition takes place in the regions lying above the curves with fixed values of T_0, when the temperature of the hot gas T_c is higher than the critical temperature T_{c*}(Bi). For $T_c < T_{c*}$, intermediate conditions between ignition and spontaneous ignition are produced.

An asymptotic solution has been described[86,87] for the problem of the heterogeneous-exchange ignition of a substance when a heterogeneous reaction of zeroth order takes place, and the results of studies[10,22,23,32-37] in which various approximate methods were used have been summarised. Experimental data[32] on the purely heterogeneous ignition of a composite fuel are given in Fig.16 in linearised form. The constants E and Qk_0 obtained differ considerably from those found in Ref.32.

The solution of the problem of the ignition of a substance when successive and parallel reactions take place in it is also of undoubted interest. The examination of this problem extends the theory of the influence of multi-stage chemical reactions on the regular features of the ignition process. An asymptotic analysis and analytical solution of these problems have been given.[88-90] The thermal theory of ignition has also been used to analyse the ignition of gas systems. In Ref.91, numerical integration using a computer was used to study the regular features of the ignition of gases by a heated surface when a single-stage reaction takes place and with allowance for diffusion and hydrodynamic phenomena. An asymptotic analysis made it possible to study this problem without allowance for hydrodynamic factors.[92] The most general asymptotic solution of the problem of the ignition of gases by a heated surface without allowance for hydrodynamic factors when successive two-stage and parallel N-stage reactions take place was obtained in Ref.93, which generalises the results of Ref.92 to the case of multi-stage reactions.

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The aspects of the thermal theory of ignition examined in the present review do not exhaust existing problems of the ignition of condensed systems, particularly for the case of the diffusion and hydrodynamic phenomena accompanying a multi-stage chemical reaction. The actual ignition of solid fuels is generally extremely complex, and cannot be described within a single theory of gas-phase, heterogeneous, or solid-phase ignition. Attempts are therefore now being made to develop a single theory taking account of reactions in the gas and solid phases, and also at the surface of a solid fuel.[94,95] The constructive ideas of the intermediate asymptote of a non-stationary ignition process, described in Ref. 96, may prove extremely useful in the study of these questions.

The thermal theory of ignition, in which no account is taken of the gas phase, generally does not make it possible to predict the influence of the surrounding medium. In the ranges of existence of non-degenerate conditions and at low thermal flux densities and high concentrations of oxidant in the surrounding medium, however, the inert warm-up is appreciably greater than the time of diffusion and chemical reaction, so that good quantitative agreement is obtained between the ignition delay times determined experimentally and calculated from the thermal theory.[97] The method of compound asymptotic expansions has been used successfully for the practical solution of problems of the thermal theory of ignition. This makes possible an optimistic approach to the study of the more complex and promising problems of the ignition of condensed and gaseous reacting systems.

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The Photochemistry and Photophysics of Spiropyrans

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The results of studies on the structure and nature of the electronic states of spiropyrans (SP) and the products of their photochromic reactions as well as the mechanism of the dissociation of the $C_{spiro}-O$ bond and the formation of a coloured form of the SP are surveyed and analysed. Also analysed are the mechanisms of the α-dissociation and predissociation of the bond, which make it possible to explain satisfactorily the dependence of the quantum yield of the photocolouring reaction on the structure of the SP, the nature of the matrix, and temperature. The prospects for the utilisation of the photochromic SP are discussed.

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I. INTRODUCTION

The photochromic spiropyrans (SP) have continuously attracted the attention of investigators. By virtue of their unique properties, they have been finding increasing applications. This is also promoted by the fact that the photochromic properties of SP are manifested in virtually any matrix—in the pure compound (in the crystalline or amorphous state), in solutions, and in polymers, and the conditions under which these matrices exist can vary over a wide range of temperature, viscosity, external pressure, and electric and magnetic field strengths. This makes it possible to employ SP as test objects in the study of the properties of the medium and of the mechanisms of its influence on the intramolecular photophysical and photochemical processes.

Spiropyrans are already used to prepare reusable polymeric photochromic materials or variable density light filters,[1-9] but their application for these purposes is limited by the low light sensitivity of the photomaterials and because enough cyclic information recording and deletion processes cannot be achieved. Apparently in the future SP will also be applied in other equally important fields. For example, it has been reported that they can be used as photoregulators of the ionic conductivity of membranes,[10] as modulators of the intensity of the fluorescence of monolayers,[11,12] etc. Presumably in the near future they will be used as elements in electronic circuits acting at the molecular level.[13,14]

Since the publication of the authors' earlier review,[15] numerous communications concerning the study of the photochromic reactions of SP and their structure have appeared. The fairly large amount of the data which have accumulated and, what is most important, its significance for the understanding of the photochemistry and photophysics of SP urgently require a critical analysis and a survey of the entire set of the results available.

As before,[15] in the analysis of the results of the studies of the primary photochemical processes as a function of the structure of the SP and external conditions, the SP are regarded as representatives of a specific class of organic compounds containing heteroatoms and belonging to the ($\sigma\pi nl$) type in terms of the orbital classification of electronic states.[16-19]

Analysis of the experimental results has shown that the photochemical activity of SP and their luminescence characteristics are determined by the position of the energy levels and the orbital nature of the lowest electronically excited states. Furthermore, in order to understand the mechanism of the photodissociation of the bond in SP, it is essential to take into account the degree of involvement of the electrons of the heteroatoms in the configuration of the electronically excited states and also the interaction of the electronic orbitals of the mutually orthogonal heterocycles in both ground and excited states.

The SP photocolouring reaction can be represented schematically as follows in a general form:[6,15]

$$A \overset{h\nu}{\rightleftarrows} A^{*} \xrightarrow{\varphi_d} X \xrightarrow{\varphi} B\,, \tag{1}$$

where A is the colourless initial spiro-form of the SP, A^* its electronically excited state, X the *cis*-cisoid isomer of the coloured form arising after the dissociation of the bond and still preserving the orthogonality of the heterocycles, B the planar coloured form of the SP, ϕ the quantum yield in the formation reaction of the B form, and ϕ_d the quantum yield in the bond dissociation process. The recombination reactions of the photoproducts with transition to the initial state and also the possible pathway leading to the formation of the B form without the formation of the intermediate X isomer are not shown in Scheme (1).

The chemical structure of the SP considered in the review are presented in Tables 1 and 2. Table 1 also lists the known quantum yields of the SP colouring reaction under the influence of light with λ = 313 and 365 nm (ϕ_{313} and ϕ_{365} respectively). The yields ϕ were determined in weakly polar solvents at temperatures close to room temperature. The total number of SP investigated for which the values of ϕ are known is much greater;[6,9,15,20-35] Table 1 includes only some SP with characteristic structures and substituents. The yields ϕ in different matrices (for certain SP) are presented in Table 3.

II. THE NATURE OF THE ELECTRONIC STATES OF SPIROPYRANS AND THE PRODUCTS OF THEIR PHOTOCHROMIC REACTIONS

1. The Structure of Spiropyrans and Their Photoproducts

The structures of more than ten SP, including the strucures of the coloured forms,^{38} have now been investigated y X-ray diffraction (XD).$^{36-41}$ The XD data show that n almost all the SP investigated the angle between the heterocycles is 90°. However, the heterocycles themselves are non-planar—the angle of the bend in the planes of the indoline ring system along the C(3)–N(1) line is 23–30° and the angle in the bend in the benzopyran ring system along the C(3′)–O(1′) line is 11–17°,^{38} depending on the ring substituents.

Table 1. The structure of spiropyrans and the quantum yields of the photocolouring reactions.

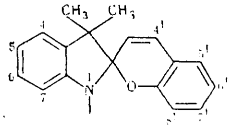
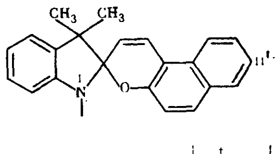
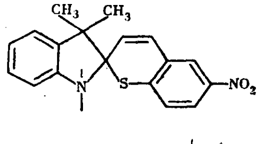
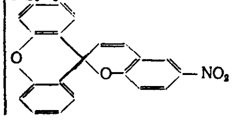
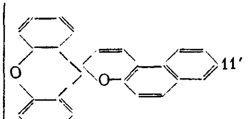
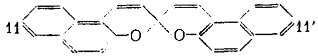
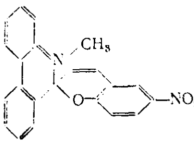
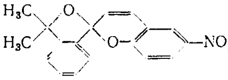
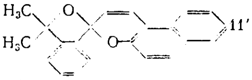
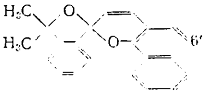
SP	Structure of SP and substituents	Solvent	φ_{313}	φ_{365}	Refs.
					
SP$_1$	1-CH$_3$	hx, t	0.1	—	[6, 15]
SP$_2$	1-CH$_3$-6′-Br	t	0.03	—	[22]
SP$_3$	1-CA$_3$-6′-NO$_2$	t	—	0.76	[20, 21]
„	»	ea	0.40	0.60	[20, 21]
SP$_4$	1-CH$_3$-6′-NO$_2$-8′-OCH$_3$	t	—	0.59	[21, 23]
„	»	d, ea	0.30	0.45	[6, 15]
SP$_5$	1-C$_6$H$_5$-6′-NO$_2$-8′-OCH$_3$	ea	0.10	0.45	[15, 26]
SP$_6$	1-CH$_3$-6′-NO$_2$-8′-C$_3$H$_5$	ea	—	0.55	[26]
SP$_7$	1-C$_6$H$_5$-6′-NO$_2$-8′-Br	ea	—	0.45	[26]
SP$_8$	1-C$_6$H$_5$-8′-NO$_2$	ea	—	0.13	[26]
SP$_9$	1-CH$_3$-6′-Cl-8′-NO$_2$	ea	—	0.05	[26]
SP$_{10}$	1-CH$_3$-4,5-benzo-6′-NO$_2$	ea	—	0.025	[26]
SP$_{11}$	1-CH$_3$-5-NO$_2$	hp	—	0.56	[21, 25]
SP$_{12}$	1-CH$_3$-5-NO$_2$-6′-OCH$_3$	hp	—	0.60	[21, 25]
„	»	t	0.36	0.60	[21, 25]
„	»	ea	—	0.33	[21, 25]
SP$_{13}$	1-CH$_3$-5′,7′-dichloro-6′-NO$_2$	d	0.47	0.58	[6]
„	»	t	0.45	0.55	[6]
SP$_{14}$	1-CH$_3$-6′-NO$_2$-8′-Br	–	—	—	—
SP$_{15}$	1-CH$_3$-5-CH$_3$CO-6′-NO$_2$-8′-OCH$_3$	t	—	0.24	[9]
SP$_{16}$	1-C$_2$H$_4$OH-6′-NO$_2$	–	—	—	—
SP$_{17}$	1-C$_2$H$_4$-O-CO-C$_3$H$_5$-6′-NO$_2$	–	—	—	—
SP$_{18}$	1-C$_{18}$H$_{38}$-6′-NO$_2$	–	—	0.45	[11]
SP$_{19}$	1-C$_4$H$_9$-6′-NO$_2$	–	—	—	—
SP$_{20}$	1-C$_2$H$_4$-2-O-CO-CH(CH$_3$)$_2$-NO$_2$	–	—	—	—
					
SP$_{21}$	1-CH$_3$	t	0.07	0.27	[22]
„	»	mch	0.06	—	[6]
SP$_{22}$	1-CH$_3$-11′-NO$_2$	t	—	0.60	[27]
SP$_{23}$	1-C$_6$H$_5$-11′-NO$_2$	t	—	0.08	[27]
					
SP$_{24}$	1-CH$_3$	t	—	~0.2	[34]
SP$_{25}$	1-C$_6$H$_5$	t	—	~0.3	[34]
SP$_{26}$		t	—	⩽0.1	[21]

Table 1 (contd.).

SP	Structure of SP and substituents	Solvent	φ_{313}	φ_{365}	Refs.
SP$_{27}$		t	0.45	0.45	[22]
SP$_{28}$	11′-NO$_2$-SP$_{27}$	t	—	0.08	[27]
SP$_{29}$		t	0.55	0.07	[22]
SP$_{30}$	11,11′-di-NO$_2$SP$_{29}$	d	—	0.59	[6]
SP$_{31}$		t	—	0.03	[31]
SP$_{32}$	7′-OCH$_3$SP$_1$	t	0.03	—	[35]
SP$_{33}$	7′-NO$_2$-SP$_1$	ea	—	0.17	[26]
SP$_{34}$		tip	0.30	0.25	[33]
SP$_{35}$		tip	0.60	0.03	[33]
SP$_{36}$	11′-NO$_2$-SP$_{35}$	tip	—	0.40	[33]
SP$_{37}$		tip	0.55	0.12	[33]
SP$_{38}$	6′-NO$_2$-SP$_{37}$	tip	—	0.40	[33]

Notation: t = toluene, d = dioxan, ea = ethyl acetate, hx = hexane, mch = methylcyclohexane, hp = heptane, and tip = t : 1 toluene–isopentane mixture.

Table 2. The lengths of the dissociating bonds (r) in spiropyrans and the activation energies (E_a^*) for the thermal bond dissociation reaction.

SP	r, Å	E_a^*, kcal mol^{-1}	Refs.
SP$_1$	—	10	[35]
SP$_2$	—	9.3	[35]
SP$_3$	1.486	12	[35, 39]
SP$_8$	1.492	7.6	[35, 36]
SP$_9$	1.497	8.5	[35, 37]
SP$_{11}$	1.453	13	[35, 38]
SP$_{14}$	1.495	—	[38]
SP$_{21}$	—	7.8	[35]
SP$_{22}$	—	8.0	[35]
SP$_{23}$	1.462	9.4	[35, 38]
SP$_{25}$	1.487	—	[40]
SP$_{27}$	—	7.4	[35]
SP$_{32}$	1.471	6.1	[35, 38]
SP$_{33}$	—	6.0	[35]
SP$_{34}$	1.454	15	[35, 41]
SP$_{35}$, SP$_{36}$	—	8.1	[35]
SP$_{37}$	1.444	—	[38]
SP$_{38}$	1.465	—	[38]

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*The activation energies E_a were determined in a matrix comprising the given compound—the melt or the amorphous vitreous state of the SP.

It is of interest to compare the length of the dissociating bond r with the activation energies E_a for the thermal bond dissociation in SP and the quantum yield in the photocolouring reaction (Tables 1 and 2). The values of E_a for all

SP with the exception of SP_{32} and SP_{33} are correlated with r: as a rule, E_a falls with increase of r. The introduction of substituents in the 7′-position stabilises the coloured form of the SP as well as the E_a as a result of the conjugation of the substituent orbitals with the π orbital of the central carbon atom.[7,35,38] The correlation between E_a and r is a consequence of the fact that the dissociation of the bond in the thermal reaction proceeds via the ground electronic state of the vibrationally excited SP.

Table 3. The quantum yields ϕ_{365} for spiropyrans in various media*.

Medium**	SP					
	SP_3	SP_{12}	SP_{13}	SP_{21}	SP_{22}	SP_{27}
Toluene (2.38)	0.76	0.60	0.55	0.27	0.60	0.45
Dioxan	—	—	0.58	—	—	—
CCl_4	0.73	—	—	—	—	—
Ethyl acetate (6.02)	0.60	0.33	—	—	—	—
1-Propanol (20.1)	0.14	0.06	—	—	—	—
Ethanol (24.3)	0.12; 0.01 (77 K)	—	0.31	0.30	0.05	0.5
Acetonitrile (36.2)	0.06	0.05	0.107; 0.43***	—	—	—
Dimethylformamide (36.7)	0.10	0.08	—	0.2	—	—
Polystyrene	0.7; 0.1 (77 K)	0	—	0.02 (77 K)	0.3	0.2 (77 K)
Poly(methyl methacrylate)	0.31; 0.07 (77 K)	0	—	—	—	—

*With the exception of specially noted cases, the temperature was close to room temperature. The yields ϕ_{365} were taken from Bertelson[6] for SP_{13}, from Reeves and Wilkinson[29] for SP_3 in PMMA at room temperature, and from Kholmanskii[22] and Kholmanskii and Tarasov[24] in the remaining cases.

**The dielectric constant ε is indicated in brackets.

***The quantum yield of the sensitised colouring reaction.

On the other hand, there is no correlation between ϕ and r. This shows in its turn that the photodissociation of the bond in the SP proceeds via the electronically excited state of the SP whose orbital nature determines the mechanism and the quantum yield ϕ of the SP photocolouring reaction. Therefore, in predicting the photochemical activity of the SP from XD data, it is essential to take into account the factors which can affect the orbital nature of the excited state, the intensity of the electronic transition, and also the effectiveness of the interaction of the electrons of various heterocycles in the excited state. Such factors are in the first place the orientation of the nitro-group relative to the plane of the benzene ring and other substituents, and the spatial orientation of the l orbitals of the heteroatom and the dissociating bond as well as the heterocycles themselves.

Since the pyran ring in the SP is nearly planar and the C–O–C angle is 119°,[36–38] presumably the valence orbitals of the oxygen heteroatom are sp^2-hybridised.

In the indoline ring of the SP, the nitrogen atom is somewhat displaced out of the plane drawn through the carbon atoms linked to it (in particular by 0.26 Å for SP_{11} [38]). The valence angles between the N–C bonds in SP_{11} are 121.4°, 119.9°, and 108.8°.[38] These data suggest the sp^2-hybridisation also of the atomic orbitals of nitrogen, although it is somewhat distorted by virtue of steric factors. This is also indicated by the comparison of the structural and luminescence-spectroscopic characteristics of SP and aromatic amines in which the nitrogen atom is sp^2-hybridised.[42]

Indeed the values λ_{max} = 375 nm and $\varepsilon_{375} = 1.8 \times 10^4$ litre mol^{-1} cm^{-1} [21,25] for the first absorption band in the spectrum of the SP having the nitro-group in the indoline ring (SP_{11}) are virtually identical with the corresponding values for p-nitroaniline and NN-dimethyl-p-nitroaniline (376 nm and 1.6×10^4 litre mol^{-1} cm^{-1} for the former and 388 nm and 1.8×10^4 litre mol^{-1} cm^{-1} for the latter[43]). We may note that the agreement between the spectra and phosphorescence decay times for SP_{11} and nitroaniline[44] also indicates the similarity of the electronic structures of the T_1 states of these compounds.

In order to determine the structure of the coloured form of the SP, IR spectroscopic,[7,45] Raman spectroscopic,[46] and photoelectron spectroscopic[47] methods were resorted to in addition to XD. Studies,[9,48–58] including, for example, polarisation measurements,[51–54] measurements of the dipole moments of the coloured molecules,[56,57] and quantum-chemical calculations,[58] have also been devoted to the investigation of the structure and properties of the coloured form and its isomers.

2. Luminescence-Spectroscopic Characteristics of Spiropyrans

The study of the orbital nature of the electronically excited states had as its primary aim the elucidation of the degree of involvement of the electrons of the heteroatoms in the electronic configuration of the lowest excited states of the ππ* type. The orbital nature of the lowest electronically excited states of SP and their energy are determined by investigating the absorption and luminescence spectra using the theory of solvatochromism.[59,60] Methods based on quantum-chemical calculations for SP or compounds modelling their fragments have also been resorted to in order to achieve a qualitative justification.[8,58,61–63] With the aid of these calculations and the theory of solvatochromism, the charges on the heteroatoms in the excited states were estimated. For this purpose, a study was also made of the deactivation of the triplet photochemically active (PCA) state of the SP by various quenching agents and in the first place by electron donors. The optical absorption spectra of certain characteristic SP have been published.[5,21,22,26,27,64–69]

The electronic transition of the π–π* type in SP without the nitro-group can be represented as a linear combination of one electron π–π* (in the aromatic system) and l–π* (electron transition from the heteroatom to the π* orbital of the aromatic system) transitions and can be designated by πl–π*.[15,18,19]

Calculations have been made for the electronic transitions and the distribution of the electron density in the S_0, S_1, and T_1 states of SP_1 has been evaluated by the CNDO method.[61] The calculated transition energies as well as the assignment of the first transition in the benzopyran ring to the π–π* type agree qualitatively with experimental data. The redistribution of electron density in the S_1 and T_1 states leads to the appearance of a positive charge on the oxygen (0.07), nitrogen (0.03), and spiro-carbon (0.017) atoms relative to the S_0 state. These results agree with the assignment of the lowest S_1 and T_2 states to the (πl, π*) type or, briefly, the L type.

On the basis of the results of theoretical calculations,[8,61,63] one can assume that the positive charge on the heteroatom of SP_1 in the S_1 and T_1 states is ~0.1. We may note that the contribution of the (l, π*) configuration to the excited state of the molecule is determined by the charge on the heteroatom.[63]

The introduction of an electron-donating substituent into the SP heterocycle leads to the appearance of an additional absorption band due to the transition involving charge transfer (CT) from the electron-donating substituent to the π^* orbital of the π-electron system.[22] The contribution of the l, π^*) configuration then diminishes and the positive charge on the oxygen heteroatom in the excited state is reduced as a result compared with the corresponding value for SP_1.[23,55]

The first transition in unsubstituted SP with the naphthopyran ring (SP_{21}, SP_{27}, and SP_{29}) is also of the $\pi l-\pi^*$ type;[22] this has been confirmed by solvatochromic studies and the presence in the absorption spectrum of bands due to stretching (1290–1350 cm^{-1}) and deformation (450–500 cm^{-1}) vibrations of the COC group.[22,64,65]

Since it is known from theoretical calculations[18,19,63] that the contribution of the (l, π^*) configuration to the excited state falls as the π-conjugation chain lengthens, presumably in the case of SP with the naphthopyran ring the positive charge on the oxygen heteroatom is smaller than for SP_1.

The introduction of a nitro-group into any of the SP fragments results in the appearance of a low-energy $\pi-\pi^*$ transition, which involves intramolecular charge transfer.[15,21,26,27,30,48,66-69] A spiropyran with the nitro-group in the benzopyran ring (A) can be designated by DSA, where D represents a heterocycle with a fairly low ionisation potential I (indoline, xanthene, benzothiazole, etc.) and C represents the spiro-carbon atom. It is known[70] that in molecules of the DSA type in which the D and A fragments are separated by three σ-bonds, apart from the local $\pi-\pi^*$ transition in the A fragment, hyperconjugation via the system of σ-bonds is responsible for the charge-transfer transition from the D to the A fragment:

$$\mathrm{DSA} \xrightarrow{h\nu} (\mathrm{D^+SA^-})^*. \qquad (2)$$

The positions and intensities of the absorption bands corresponding to the transitions in the A fragment and in process (2) are determined by the value of I for the D fragment and the electron affinity ε_A for the A fragment as well as the energy of the interaction of the (DSA*) and $(D^+SA^-)^*$ configurations.[70]

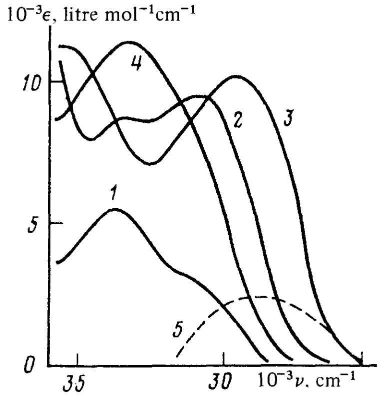


Figure 1. Absorption spectra of SP in isopentane: 1) SP_1; 2) SP_3; 3) SP_4; 4) SP_{34}; 5) difference between the absorption spectra of SP_4 and 8-methoxy-6-nitro-2*H*-chromene (MA).[68]

In SP the interaction with the π electrons of the D and A rings as a consequence of spiroconjugation[62] and the hyperconjugation of the n, σ, and π orbitals of the non-planar D and A rings in the ground state of the spiropyran can also lead to the appearance of a transition of type (2).[61]

Indeed comparison of the absorption spectra of SP having different D rings with the spectrum of the molecule modelling the A ring (MA), presented in two publications,[68,69] makes it possible to discover in the spectrum of the SP an additional absorption band whose position (ν_M^{DA}) depends on the structure of the D ring and which has an extinction coefficient ε a factor of 2–3 smaller than the band due to the transition in the A ring. The value of ν_M^{DA} for indoline SP is close to ν_M^A for the band due to the $\pi-\pi^*$ transition with charge transfer in the A ring, which is designated by $\pi l-\pi^*\pi_n^*$,[15,16,21,26] where π_n^* represents the orbital of the nitro-group and l the orbital of the heteroatom conjugated with the π system of the benzene ring[42] (Fig.1). The first absorption band in the spectra of these SP therefore constitutes a superposition of the absorption band due to the charge transfer transition in the A ring and the transition (2). Since I for the D ring in SP_{34} is greater than I for the D ring in SP_3,[70] the frequency ν_M^{DA} for SP_{34} should be greater than for SP_3. It is therefore evident that ν_M for the first absorption band of SP_{34} is greater than ν_M for SP_3 (Fig.1).

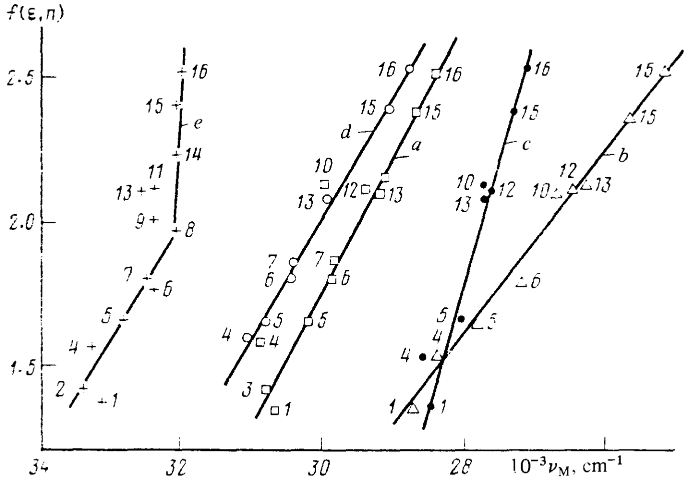


Figure 2. Dependence of the positions of the maxima of the first absorption bands of SP_3 (*a*), SP_{11} (*b*), SP_{24} (*c*), SP_{26} (*d*), and SP_{34} (*e*) on the universal interaction function $f(\varepsilon, n)$: 1) hexane; 2) isopentane; 3) cyclohexane; 4) heptane; 5) carbon tetrachloride; 6) benzene; 7) toluene; 8) chloroform; 9) tetrahydrofuran; 10) ethanol; 11) methanol; 12) acetone; 13) acetonitrile; 14) chlorobenzene; 15) dimethylformamide; 16) dimethyl sulphoxide.[66,67]

The energies of the (π, π^*) states (DSA*) and $(D^+SA^-)^*$ of spiropyran diminish as a result of general interaction with the solvent and to a greater extent than the energy of the ground state of SP.[59,60] If the molecule has no isolated orbitals, the dependence of ν_M on the dielectric constant and the refractive index is described in this case by the familiar[59] function of the general interactions $f(\varepsilon, n)$. This relation for characteristic SP is illustrated in Fig.2 (according to the data of Kholmanskii and co-workers[15,66,67]). The orbital nature of the electronic transition and the change in the dipole moment of the molecule in this transition can be determined from the qualitative and quantitative analysis of these relations. In particular, in the case of SP_{34} the presence of a break in the relation between ν_M and $f(\varepsilon, n)$ for $f \cong 2$ demonstrates the involvement of the electrons of the isolated *n* orbital of the oxygen in the oxaindan ring in the transition (2). The specific interactions of the highly polar and OH-containing solvent molecules with the *n* orbital of SP_{34} lower the ground level of this compound. As a result of the summation of the effects of the universal and specific interactions, ν_M hardly changes when $f > 2$, while under conditions where $f < 2$ the dependence of ν_M on $f(\varepsilon, n)$ for SP_{34} has almost the same slope as for SP_3, SP_4, SP_{26}, and MA (Fig.2 [69]). This indicates the similarity of the changes in the dipole moment of the SP on excitation of the transition in the A ring and in the transition (2).

However, the dipole moment changes appreciably when the oxygen heteroatom in the A ring is replaced by nitrogen (as in SP_{11}) and sulphur (as in SP_{24}) (Fig.2). Evidently, as a consequence of the changes in *I* for the D ring and ε_A for the A ring of SP_{11} and SP_{24}, the transition (2) in these SP has a significantly greater energy than the transition in the A ring.[68,70] On the basis of the dependence of ν_M on $f(\varepsilon, n)$, it is possible to estimate the charges on the heteroatoms in the DSA* states of the (π, π^*) type[21,66] which will be designated for brevity as states of the N type (Table 4).

Table 4. The orbital nature, the charges on the heteroatom (*q*), the lifetimes (τ_t), and the constants for the quenching by triphenylamine of the triplet states of spiropyrans (k_q^{TPA}) in toluene.[23,27,55,66]

SP	State	τ_t, s	k_q^{TPA}, litre $mol^{-1} s^{-1}$	*q*, *e*
SP_1	*L*	10^{-8}	$6 \cdot 10^8$	~ 0.1
SP_2	*L*	—	$< 6 \cdot 10^8$	< 0.1
SP_3	*N*	10^{-9}	$4 \cdot 10^9$	0.4
SP_7	*N*	$6 \cdot 10^{-10}$	—	—
SP_{12}	*N*	$1.5 \cdot 10^{-8}$	$9 \cdot 10^8$	0.4
SP_{22}	*L*	$< 10^{-8}$	—	$\leqslant 0.1$
SP_{22}	$(\pi, \pi^* \pi_n^*)$	10^{-6}	$3 \cdot 10^7$	$\ll 0.1$
SP_{24}	—	—	—	0.2
SP_{26}	*N*	—	—	0.4
SP_{28}	*L*	$6 \cdot 10^{-9}$	$5 \cdot 10^5$	$\leqslant 0.1$
SP_{36}	$(\pi, \pi^* \pi_n^*)$	$1.5 \cdot 10^{-8}$	10^8	$\ll 0.1$
SP_{38}	$(\pi, \pi^* \pi_n^*)$	$2 \cdot 10^{-8}$	$6 \cdot 10^7$	$\leqslant 0.1$

In SP with the naphthopyran ring containing the nitro-group, the first electronic transition is of the $\pi - \pi^* \pi_n^*$ type.[27] The involvement of the *l* electron in excitation is improbable[18,27] and the charge on the nitro-group is transferred mainly from the naphthalene ring.

All the SP with the nitro-group phosphoresce at 77 K.[6,21,27,66] In addition, the fluorescence of SP_{19} in liquid solution at room temperature has been observed.[71] The phosphorescence spectrum of SP_3 has a vibrational structure. It follows from its analysis, carried out by Khamchukov et al.[72] and Gehrtz et al.,[73] that the stretching (symmetrical) and deformation vibrations of the nitro-group are manifested in the spectra. The frequencies of these vibrations differ appreciably for SP and MA.[68] The 0–0 transition frequency ν_{00} in the case of the phosphorescence of SP with the nitro-group in the benzopyran ring can be both greater and smaller than the ν_{00} for the phosphorescence of the corresponding nitrochromene, depending on the structure of the D ring.[68,69] For example, for SP of the type of SP_3 and SP_4, the frequency ν_{00} is greater by ~700 cm^{-1} than for the phosphorescence of the corresponding MA and the quantum yield ϕ_{ph} of the phosphorescence of the SP exceeds by a factor of three that for the MA.[69] These differences are apparently caused by the interaction of close levels of the (DSA*) and $(D^+SA^-)^*$ singlet and triplet states of the SP.

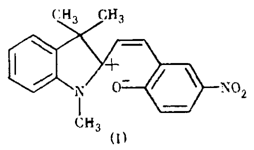
The position of the 0–0 band in the phosphorescence spectra of spiropyrans with the nitro-group is almost independent of the nature of the solvent.[6,29,48,72,73] On the other hand, in the case of SP_2 this band undergoes a hypsochromic shift by ~2000 cm^{-1} on replacement of the non-polar matrix by a polar one or by a hydroxylated matrix.[29,48] The phosphorescence lifetime of SP having the nitro-group and the corresponding nitrochromenes varies from ~0.03 to 0.3 s. The phosphorescence excitation spectrum of SP_3 coincides with the absorption spectrum within the limits of the first absorption band in solvents of the type of petroleum ether, propanol, and tetrahydrofuran (THF).[30,72] These results make it possible to assign the phosphorescence state of SP with the nitro-group in the benzopyran ring to the ^3N type and in the case of SP_2 to the ^3L type.

The high values of the intersystem inversion constant K_{ST} for SP with the nitro-group are due to the presence of intermediate $^{1,3}(n, \pi^*)$ levels of the nitro-group, at least one of which is located between the $^{1,3}N$ levels.[15,66,68,74,75] The constant K_{ST} can reach in this instance ~10^{11} s^{-1}.[16-18,74] It follows from the analysis of the experimental data for nitroanisoles, epoxynitroindalone, and nitronaphthalenes[76-78] and from theoretical calculations that the energy of the $^1(n, \pi^*)$ level for SP with the nitro-group is ~27500 cm^{-1} and that of the $^3(n, \pi^*)$ level is 23500 cm^{-1}–24500 cm^{-1}.

The fluorescence of the spironaphthopyrans SP_{22}, SP_{23}, and SP_{28} arises from the $^1(\pi, \pi\pi_n^*)$ state and the simultaneous presence of both fluorescence and phosphorescence shows that the $^{1,3}(n, \pi^*)$ levels of the nitro-group lie above the energy level of the $(\pi, \pi^*\pi_n^*)$ state.[27,79,80] The sharp differences between the fluorescence and phosphorescence intensities of SP_{22}, SP_{23}, and SP_{28} indicate different positions of the ^3L and $^3(\pi, \pi^*\pi_n^*)$ levels in these compounds and hence a different nature of the phosphorescent states.

Only fluorescence is observed for SP without the nitro-group (SP_1 and SP_{21}),[65,81,82] but one can postulate that the lowest triplet level of SP_1 has an energy close to that of the phosphorescent level of SP_2.

The following facts are known about the luminescence-spectroscopic characteristics of the SP photoproducts. The coloured form (*B*) exhibits only an intense fluoroescence.[6,7,15,30,49] In a study[73] of the photocolouring reaction of SP_3 at $T \leqq 4.2$ K, which stops at the state involving the formation of the *cis*-cisoid isomer *X*, the phosphorescence band of the *X* isomer has been discovered (at ~15000 cm^{-1} in trimethylpentane and n-hexane). The formation of this isomer has been confirmed by the method involving the optically detectable magnetic resonance, whose use together with theoretical calculations made it possible to investigate the structure of the *X* isomer and to represent it in the following form:



(I)

It has been established by studying the photocolouring reactions of SP at low temperatures and in the matrix comprising the compound itself that an absorption band whose frequency is close to the absorption band of the thermodynamically more stable *trans*-isomer of the *B* form corresponds to the *cis*-cisoid isomer of the *B* form of SP such as SP_3 or spironaphthopyrans with and without the nitro-group.[6,35,49,50,54,80]

. Spectrokinetic Studies on Photochromic Transformations f Spiropyrans

The spectrokinetic studies on photochromic reactions of SP, carried out under both photostationary conditions and with the aid of pulse (mainly laser) techniques proved fruitful for the elucidation of the orbital nature and the energy of the PCA state of the SP and for the determination of the photocolouring reaction mechanism. We shall not dwell on a large number of studies of the kinetics of the reactions of the coloured form of SP in which the influence of the structure of the SP and the nature of the matrix on the rate constant for the dark decolorisation of the *B* form[55,83–89] and the molecular association processes of the SP in both *A* and *B* forms were investigated.[74,83,90–97] The association effects significantly complicate the pattern of the photochromic reactions of the SP, particularly in aliphatic solvents and at high SP concentrations but do not influence appreciably the primary intermolecular photophysical and photochemical processes over a wide range of SP concentrations (10^{-6}–10^{-4} M)[97] in weakly polar solvents.

We shall analyse in the first place the results of the study of the quenching of the photocolouring reactions of SP by various quenching agents under photostationary conditions. These studies were performed to elucidate the question of the involvement of the triplet state of the SP in the photocolouring reaction and to determine its orbital nature.

The following results were obtained in experiments on the quenching of the photocolouring reaction by molecules with a low energy of the *T* state (anthracene, etc.) and electron donors. The reaction involving the photocolouring of SP having the nitro-group in the indoline and naphthopyran rings in weakly polar solvents proceeds 100% via the triplet state, while in SP with the nitro-group in the benzopyran ring it proceeds via this state to an extent not less than 70%.[23,27,29,98,99] The results of the estimation of the lifetimes of the lowest triplet states of SP (including PCA) are presented in Table 4. The quenching of the SP photocolouring reaction by electron donors is due to the deactivation of the triplet state as a result of electron transfer in a triplet exciplex between the SP and the electron donor.[23,99,100–102]

The quenching rate constant k_q depends on *I* for the electron donor and ε_A for the spiropyran in the excited state. For example, for tetramethyl-*p*-phenylenediamine (TMPP), it is close to the diffusion rate constant regardless of the SP structure.[23] Conclusions concerning the orbital nature of the deactivated triplet state of various SP have been reached from a comparison of the k_q for the same electron donor having a higher *I* than TMPP. These data for the case where the quenching agent was triphenylamine are listed in Table 4, from which it follows that k_q^{TPA} is correlated with q. The contribution of the (l, π^*) configuration to the *T* state of the SP of the corresponding type and the electron affinity ε_A are determined by the positive charge q on the heteroatom. The negative charge is in this case localised on the nitro-group and ensures, for example, the effective formation of hydrogen-bonded complexes between the proton-donating additive in the SP or another aromatic nitro-compound in the excited state.[6,76,103,104]

The low values of τ_T (Table 4) are due to the rapid intramolecular deactivation of the triplet state as a result of the reaction yielding the coloured form. This evidently also

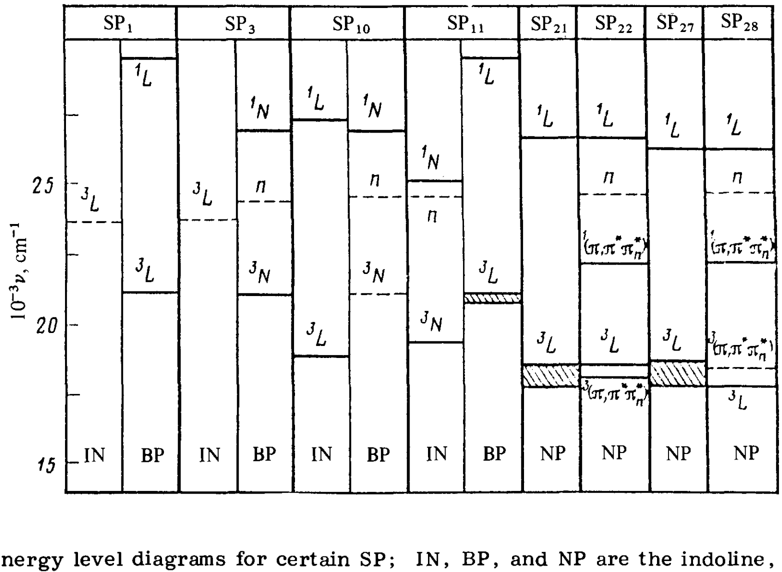


Figure 3. Energy level diagrams for certain SP; IN, BP, and NP are the indoline, benzopyran, and naphthopyran rings of the SP.[66]

accounts for the absence of an influence of added oxygen and cyclo-octatetraene[15,71] on ϕ at concentrations of additives of $\sim 10^{-3}$ and 10^{-2} M respectively. Such concentrations are insufficient for the observation of an appreciable influence by the quenching agent on the photocolouring reaction of the SP with the nitro-group in the benzopyran ring.[23,102]

Thus experimental studies have shown that both the singlet (for SP without the nitro-group) and triplet (for SP with the nitro-group) PCA states should include a definite contribution by the (l, π^*) configuration. This contribution determines the positive charge on the heteroatom in the D and A rings and, as will be shown below, the mechanism and the effectiveness of the dissociation of the C_{spiro}–O bond depend in their turn on the latter. The probability of the population of the levels of the PCA states depends significantly on the relative positions of the electronic levels of the SP. Data[15,22,27,29,68,105–107] concerning the disposition of the electronic levels of the various fragments of the SP molecule make it possible to construct a diagram of the lowest electronic levels for SP with certain characteristic structures and substituents (Fig. 3 [66]). The suggested disposition on the diagram of the levels which had not been observed experimentally is shown by dashed lines. Levels of the $^{1,3}(n\pi^*)$ type have been conventionally represented by a single level designated by n, and this also applies to the levels of the (DS*A) and $(D^+SA^-)^*$ states of SP_3, which are represented by a single N level.

III. THE MECHANISM OF THE PHOTOCOLOURING REACTION

The principal question concerning the mechanism of the photodissociation of the C_{spiro}–O bond and the formation of the B form is how the redistribution of electron density arising on excitation of the π-electron system of the SP ensures the weakening of the C_{spiro}–O σ-bond and what role the vibrational excitation of the SP molecule plays in the bond dissociation.

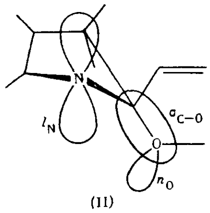
The intramolecular photophysical and photochemical processes are unambiguously determined by the orbital nature of the electronically excited state of the SP, which specifies the initial redistribution of electron density, regulating both the mechanism of the interaction of the electrons of the C_{spiro}–O σ-bond with other electrons of the molecule and the mechanism of the excitation of particular vibrations in the molecule. The orbital nature of the electronically excited state of the SP is determined in its turn by its molecular structure. For this reason, the elucidation of the mechanism of the bond photodissociation makes it possible to relate directly the effectiveness of the photocolouring of the SP to the structure, i.e. permits the specific synthesis of SP with particular photochromic properties.

1. The Mechanism of the α-Dissociation of the C_{spiro}–O Bond

The quantum yields of the photocolouring reaction of SP with the nitro-group in the indoline ring are fairly high and comparable to the ϕ for SP with the nitro-group in the benzopyran ring (Table 1). On the other hand, the energy of the electronic excitation of these SP on irradiation with light at the wavelength corresponding to the first absorption band is fully localised in the indoline fragment regardless of the type of substituent in the benzopyran ring (Fig. 3 [21,25]).

For SP with an analogous disposition of the levels but with a different orbital nature of the lowest triplet state, the values of ϕ are significantly smaller than for SP of the SP_3 type (cf. with SP_{10} in Fig. 3 and in Table 1). The principal difference between the orbital nature of the lowest triplet state of these SP consists in a much greater positive charge on the nitrogen heteroatom in the ^3N state of SP of the SP_{11} type than in the ^3L state of SP of the SP_{10} type.

On the basis of data for the structure of SP (see Section II), their central part can be represented as follows:



(II)

Here the axis of the l orbital of oxygen is perpendicular to the plane of the figure. It follows from XD data for SP that the solid angle between the l_N orbital and the σ_{C-O} bond is 10–30°. Bearing in mind their close proximity, one can postulate the interaction of the electrons of these orbitals. In the gound state of the SP, such interaction is referred to as the anomeric effect.[21,108] Its essential feature consists in the mixing of the l_N orbital and the unoccupied antibonding σ^*_{C-O} orbital. As a result of this interaction, the C_{spiro}–O bond is weakened even in the ground state.[36–41]

We shall now discuss the orbital nature of the N-type triplet PCA state of SP_{11}. It follows from Section II, that the luminescence-spectroscopic characteristics of SP with the nitro-group in the indoline ring virtually coincide with the corresponding characteristics of p-nitroanilines and are close to the characteristics of p-cyano-N,N′-dimethylaniniline.[109] For the latter compound it is known[110] that the dipole moments of the molecule in the ^1N state ("b") and in the biradical state with "twisted" configuration ("a") are virtually identical. This makes it possible to represent the structure of the precursor of the state "a", namely the Franck–Condon state "b", also in the form of a biradical in which the unpaired electrons are localised on the nitrogen atom of the CN group.

Taking into account these data and using the one-electron approximation, the N-type Franck–Condon state of SP_{11}, in which there is an appreciable positive charge on the nitrogen atom, can also be represented by a biradical. Consequently the l_N orbital in the $^{1,3}N$ states of SP_{11} has a radical character and this leads to the exchange interaction of the electrons of the l_N and σ_{C-O} orbitals, which constitutes the basis of the mechanism of the α-dissociation of the bonds (type 1 Norrish reaction[19,20,100]). The vibrationally excited radical-cations of amines and various carbonyl compounds dissociate according to this mechanism.[19,100,111–113] In SP of the SP_{11} type, the vibrational excitation of the spiro unit (II) is also essential for the dissociation of the C_{spiro}–O bond via the α-mechanism.[113] Under these conditions, the most effective are the low-energy deformation vibrations of one heterocycle relative to the other, in which the solid angle between the axes of the l_N and σ_{C-O} orbitals diminishes. The torsional vibrations of the heterocycle are less effective in this respect, although their excitation can increase sharply the probability of the non-radiative relaxation of the electronically excited state of the SP [114] with formation of the B form.

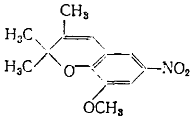
Together with the dissociation of the C–O bond, the dissociation of the C_{spiro}–C(3′) bond in SP with the nitro-group in the indoline ring can also dissociate via an analogous mechanism. Presumably this reaction ensures the irreversible decomposition of the given SP which has a lower photostability than SP with a nitro-group in the benzopyran ring.[115]

The effectiveness of the dissociation of the C_{spiro}–O bond via the α-mechanism is fully determined by the electronic structure of the indoline ring in the ^3N state. The introduction of various substituents into the benzopyran fragment of an SP containing the nitro-group in the indoline ring has virtually no effect on the yield ϕ.[21,25,102]

Since, like the nitro-group, the acetate group is an electron-accepting substituent, its introduction into the 5-position renders the lowest triplet state a highly polar CT state. It follows from the data of Gal'berstshtam and co-workers[9,89] that the disposition of the electronic levels of SP_{15} is analogous to that in SP_{11}. Taking into account these data, it is possible to postulate also for SP_{15} a mechanism for the α-dissociation of the C_{spiro}–O bond, which explains the fairly high value of ϕ_{365} for this SP (0.24) compared with ϕ_{365} for SP_{10} (Table 1).

Thus the α-dissociation mechanism, well known in the photochemistry of organic compounds, makes it possible to explain the high effectiveness of the cleavage of the C_{spiro}–O bond in the formation of the *B* form of SP with an electron-accepting substituent in the indoline ring.

We shall consider the mechanism of the photodissociation of the bond in indoline SP with the nitro-group in the benzopyran ring and SP with other D and A rings (xanthene, oxaindan, etc.). Before doing this, we may note that the mechanism of the bond cleavage in the MA



(III)

proceeds to the extent of 80% via *N*-type *T* state and the quantum yield of the *B* form of compound (III) is 0.7.[116] On this basis, one can assume that the (DS^3A^*) state of SP is likewise a PCA state. Furthermore, in the case of indoline SP with the nitro-group in the benzopyran ring, the positive charge is localised in the $(D^+SA^-)^*$ states on the nitrogen atom of the D ring,[28,117,118] while the negative charge is localised on the nitro-group.[103,118,119] Consequently the electronic structure of the given states ensures bond dissociation via the α-mechanism. Thus the high values of ϕ for the spiropyrans of SP_3 type are due to the fact that both lowest ^3N states of the (DSA^*) and $(D^+SA^-)^*$ types are PCA states and that the photocolouring reaction proceeds via the mechanism

$$\begin{tikzcd}
 & (DS^1A^*) \arrow[r] \arrow[dd] & (DS^3A^*) \arrow[dd] \arrow[dr] & \\
DSA \arrow[ur, "h\nu"] \arrow[dr] & & & B \\
 & {}^1(D^+SA^-)^* \arrow[r] & {}^3(D^+SA^-)^- \arrow[ur] &
\end{tikzcd} \qquad (3)$$

The probability of bond dissociation on excitation in the PCA states of SP is determined by the charge *q* on the oxygen and nitrogen atom. The latter depends in its turn on the change in the dipole moment of the molecule, which is correlated with the dipole moment of the transition |M| for transitions with intramolecular CT.[15]

The value of |M| is related to the experimental characteristics of the CT band:[120]

$$|M| = 0.0958\,(\Delta\nu_{1/2}\varepsilon_M\nu_M^{-1})^{1/2}, \qquad (4)$$

where $\Delta\nu_{1/2}$ is the half-width of the CT band. Assuming that ϕ is proportional to *q*, it is possible to obtain with the aid of Eqn.(4) the relation between ϕ and the intensity of the first absorption band of the SP with the nitro-group. Fig.4 presents the dependence of ϕ on $(\varepsilon_M\nu_M^{-1})^{1/2}$ for a series of SP. Its linearity demonstrates the validity of hypotheses[15,21,102] concerning the dependence of the mechanism of the photodissociation of the bond in SP on its structure.

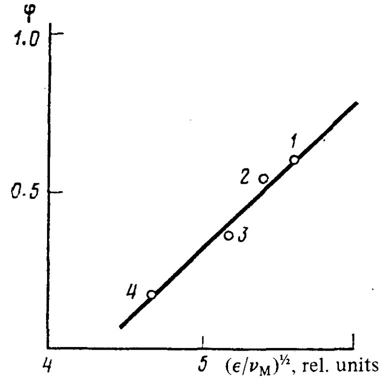
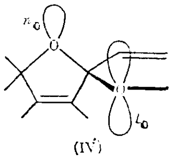


Figure 4. Dependence of ϕ on $(\varepsilon/\nu_M)^{1/2}$ for different SP: 1) SP_3; 2) SP_6; 3) SP_{33}; 4) SP_8 (the values of ε and ν_M have been taken from Kholmanskii et al.[15]).

The occurrence of the transition (2) and the corresponding states $(D^+SA^-)^*$ in SP of the SP_3 type makes it possible to explain readily the dependence of the probability of the photoionisation of the SP on its structure in the presence of an external electron acceptor.[28,117,121,122] Scheme (3) can also be used successfully to account for the intra- and intermolecular photochemical processes occurring on UV irradiation of an SP_8 single crystal at 77 K,[123,124] since the key factor in these studies was the assumption of the formation of the $^3(D^+SA^-)^*$ states via the tunnel electron transition between the D and A rings in the (DSA^*) state of the SP. The orbital nature of the (DSA^*) state ensures, with the corresponding probability, the α-dissociation of the C_{spiro}–N bond, which may be the basis of the irreversible photodecomposition of SP of the SP_3 type.

On the basis of XD data for the structure of SP_{34}, its spiro-unit can be represented as follows:



(IV)

On excitation of the $(D^+SA^-)^*$ states in SP_{34}, the positive charge is localised on the oxygen atom of the oxaindan ring and its n_O orbital assumes a radical character (see Section II). Since the n_O orbital is almost orthogonal in relation to the σ orbital of the C_{spiro}–O bond [see structure (IV)], the exchange interaction between the electrons of these orbitals is unlikely. As a result, the $(D^+SA^-)^*$ states of SP_{34} are not PCA states. The lower yield ϕ for SP_{34} compared with SP_3 (Table 1) and the temperature dependence of ϕ for SP_{34} [33] show that the levels of the $^{1,3}(D^+SA^-)^*$ states are below the levels of the PCA states of the (DSA^*) type.

As in a study by the authors of the review,[27] the following scheme can be formulated for SP_{34}:

$$\begin{tikzcd}
& (DS^1A^*) \arrow[r] & (DS^3A^*) \arrow[r] \arrow[d, shift right] & B \arrow[d] \\
DSA \arrow[ur, "h\nu"] \arrow[dr] & & & \\
& {}^1(D^+SA^-)^* \arrow[r] & {}^3(D^+SA^-)^* \arrow[r] \arrow[u, shift right, "\overline{kT}"'] & DSA
\end{tikzcd} \qquad (5)$$

The energy difference ΔE between the (DS^3A^*) and ${}^3(D^+SA^-)^*$ states of SP_{34} is close to the activation energy E_a for the photocolouring reaction[27] and can be estimated by comparing the known values of E_a for other SP. E_a for SP_{34} is greater than for SP_3 (~0.04 eV) [29] but smaller than for SP_{22} and SP_{36} (~0.15 eV),[27] since $\phi = 0$ for SP_{34} at 77 K and does not change appreciably in the range 180–250 K.[33] Consequently an estimate in the range $0.04 < \Delta E < 0.15$ eV is valid for $\Delta E \cong E_a$. For such a low value of ΔE, the PCA state of the (DS^3A^*) type is effectively populated via a thermal mechanism.

The structure of the xanthone ring also fails to ensure conditions essential for bond dissociation via the α-mechanism in the $(D^+SA^-)^*$ states.[21,102] The more significant decrease of ϕ for SP_{26} compared with SP_3 (Table 1) is apparently caused by the increase of ΔE to such an extent that the thermal population of the PCA state of the (DS^3A^*) type becomes improbable and the state is almost completely deactivated owing to the transition $(DS^3A^*) \rightarrow {}^3(D^+DA^-)^* \rightarrow DSA$.

In SP of the SP_{24} type, the valence orbitals of the sulphur atom are sp^3-hybridised,[40] which diminishes the degree of their conjugation with the π-electron system of the benzene ring and the charge q in the ${}^1N$ state (Table 4). The values of I for the indoline and benzopyran rings are similar.[70] On the basis of these data, one can postulate that the levels of the $(D^+SA^-)^*$ states lie above the corresponding levels of the (DS^*A) states and that the α-dissociation of the C_{spiro}–S bond is unlikely; the photocolouring reaction of the given SP therefore proceeds with a fairly high value of ϕ via the (DS^1A^*) state[34,40] in accordance with the predissociation mechanism (see below). Thus, using the known[15,21,24,26,70,125,126] features of the changes in the intensity and energy of CT transitions (within the ring having the nitro-group and between the orthogonal rings) as a function of the structure of the SP and the nature of the matrix and also by invoking the α-dissociation mechanism, it is possible to explain successfully and to predict the photochemical activity of SP.

2. The Role of Vibrational Excitation and the Mechanism of Bond Predissociation in SP

Studies of the influence of the vibrational excitation of the electronically excited state on the kinetics of the photochemical reaction are of undoubted interest. For SP with the nitro-group, the photocolouring reactions proceed mainly via the formation of the triplet state: the vibrational excitation of the PCA state is essential to ensure the effective interaction of the orbitals of the orthogonal rings, which constitutes the basis of the α-dissociation mechanism. The energy of the electronic excitation, equal to the difference between the energies of the S_1 and T_1 states (5000–6000 cm^{-1}), may be expended on this vibrational excitation.[16,66] This excitation is also necessary to ensure that the atoms whose bond is ruptured can move apart to a sufficient distance to avoid recombination.[19]

SP with the naphthopyran heterocycle (SPN) are characterised, like their benzopyran analogues, by high yields ϕ (Table 1). However, the increase in the length of the π-electron system changes the disposition and orbital nature of the lowest electronically excited states of SPN (Table 3), as a result of which their photophysical and photochemical properties are also altered. In particular, the yields ϕ for SPN without the nitro-group depend only very slightly on th nature of the solvent and of the second heterocycle (Tables 1 and 3). This is a consequence of the photocolouring reaction of the given SP via a singlet state in accordance with a mechanism different from the α-dissociation mechanism.[22,24,27] It has been established[22] that the dissociation of the C_{spiro}–O bond in the ${}^1L$ state requires the excitation of the SPN at least to the first vibrational level of the given state. The vibrations whose nature is that of the vibrations of the COC group (see Section II) and their excitation promote the non-radiative transition $A^* \rightarrow X$ under these conditions. The same transition is evidently responsible for the decrease by a factor of two of the intensity of the fluoresence of SP_{21} on increase of the frequency of the exciting light from ν_{00} to $\nu = \nu_{00} + 500$ cm^{-1}.[65] In conformity with these features, the yield ϕ tends to zero on excitation of the SPN by light having a frequency ν close to ν_{00}.[22]

In the irradiation with light having $\lambda = 365$ nm ($\nu_{365} = 27\,400$ cm^{-1}) of the spiropyrans SP_{29}, SP_{35}, and SP_{37}, the energy of the light quantum is lower than the energy of the 0–0 transition ($h\nu_{00}$), whose frequency can be determined from the absorption spectra. For SP_{35}, SP_{29}, and SP_{37}, this frequency is 28750, 28640, and 28500 cm^{-1} respectively.[22,23] In this case the photocolouring reaction takes place because light with $\lambda = 365$ nm is absorbed by vibrationally and rotationally excited SPN molecules in the ground electronic state. Consequently ϕ_{365} for these SP should be proportional to the number $n^{\#}$ of such molecules, which is determined by the Boltzmann distribution $n^{\#} = n\exp[-\Delta\nu/kT)]$, where $\Delta\nu = \nu_{00} - \nu_{365}$.

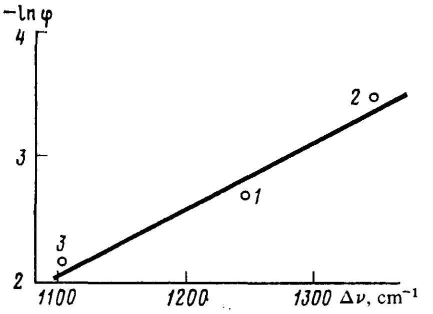


Figure 5. Dependence of $-\ln\phi$ on $\Delta\nu$ for SP: 1) SP_{29}; 2) SP_{35}; 3) SP_{37} (the values of ϕ and ν have been taken from Kholmanskii[22] and Kholmanskii and Lokshin[33]).

Thus $\ln\phi$ should be directly proportional to $\Delta\nu$. Fig.5 presents the dependence of $-\ln\phi$ on $\Delta\nu$ for a series of SPN, from the slope of which it is possible to determine T. It proved to be 250 ± 10 K, i.e. was virtually identical with the temperature at which ϕ_{365} had been determined for these SP.[22,33] The result constitutes additional confirmation that the photocolouring reaction of the SPN without the nitro-group proceeds via the ${}^1L$ state of the vibrationally excited SPN molecule. Under these conditions, light with $\lambda = 313$ nm excites either the higher vibrational levels of the S_1 state or the S_2 state is excited. The maximum value $\phi \cong 0.6$ (Table 1) is obtained in both cases. It follows from the temperature variation of ϕ for SPN with the nitro-group that E_a for the photocolouring reaction exceeds ΔE, which is equal to the difference between the energies of the ^3L-type PCA state and the lowest $^3(\pi, \pi^*\pi_n^*)$ state by ~600 cm^{-1} and is close to the frequency of the first vibrational quantum.[27]

These results suggested[22,35] that the bond dissociation in SPN proceeds via the predissociation mechanism. The role of the dissociative level is then assumed by the electronic level of the *cis*-cisoid isomer *X*, which intersects the level of the PCA state in the vicinity of its first vibrational level. The formation of the isomer *X* leads to the isomerisation mechanism for the degradation of the electronic excitation energy to vibrational energy.[6,127,128] On the basis of the results described and using the data[6,7,35] for the E_a for the forward and reverse thermal formation reactions of the coloured form of SP, it is possible to represent the path followed in the photochemical and thermal formation reactions of the isomer *X* in the *B* form by potential energy curves and the transitions between them can be illustrated (Fig.6).

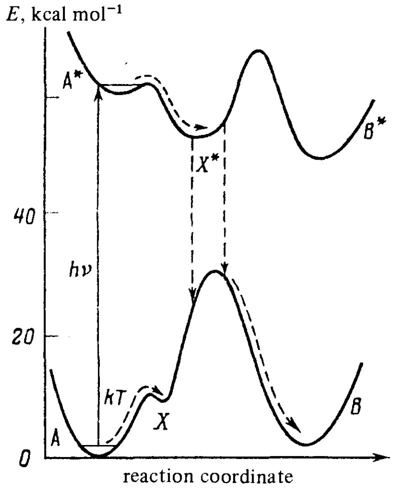


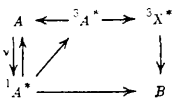
Figure 6. The potential energy surfaces for the ground and electronically excited states and the thermo- and photocolouring reaction pathways of SP [35].

3. The Nature of the Short-Lived Products arising in the Flash Photolysis or Pulse Radiolysis of Spiropyrans. The Mechanism of the Photocolouring Reaction

Numerous studies have been made of reaction (1) by the method of kinetic pulse spectroscopy (especially laser spectroscopy).[55,74,90,99,116,128–141] The time resolution of pulse apparatus has been increased at the present time to the picosecond range.[74,97,132,140] The values of λ_{max} obtained in the above studies, characterising the absorption by short-lived products, and their lifetimes are listed in Table 5.

An especially large number of studies have been devoted to SP containing a nitro-group. It has been established for SP_1 and SP_{21} [15,55,81,91,128] that the photocolouring reaction proceeds via the ^1A state. Only the absorption bands of the coloured form but not of the short-lived products are observed in the spectra of the photoproducts at least in the time range $\geq 10^{-7}$ s. The T–T absorption spectrum of SP_1 has been obtained by means of the sensitised population of the T_1 level via the T–T energy transfer mechanism.[128]

The photocolouring reaction of the nitrochromene(III) and the 3,3-dimethylpiperidine SP with the benzopyran ring has been investigated by laser flash photolysis.[116,141] The following process scheme, analogous to scheme (1), has been proposed for compound (III):



(6)

The absorption spectra of the states ^3A, ^3X, and B are similar and can be distinguished only kinetically using the differences between their lifetimes, which are 80 ns, 400 ns, and 0.1 s respectively. The quantum yields in the formation of B via ^1A and ^3A are in the ratio 1 : 4, their sum amounting to 0.7, while the quantum yield of the state ^3A is 0.7.

Table 5. Spectrokinetic characteristics of the short-lived products of the photolysis and radiolysis of spiropyrans.

SP	Method of study	Δt, s	Matrix	λ_{max}, nm	τ, s	Refs.
SP_1	l.p.	10^{-8}	ch	480	$6\cdot10^{-7}$	[128]
SP_3	f.p.	10^{-5}	t	440	$5\cdot10^{-4}$	[129]
	f.p.	10^{-6}	mch	430	10^{-3}	[130]
	l.p.	10^{-8}	mch	430	$1.5\cdot10^{-7}$	[96]
	l.p.	10^{-8}	ms	430, 600	$2.5\cdot10^{-7}$	[96]
	l.p.	10^{-9}	t	430	10^{-8}	[131]
	l.p.	10^{-9}	e	430, 570	10^{-8}; 10^{-7}	[131]
	l.p.	10^{-9}	pmma	460	—	[131]
	l.p.	10^{-11}	t, e	430, 580	10^{-9}—10^{-8}	[132]
SP_4	f.p.	10^{-4}	t	445	$5\cdot10^{-4}$	[129]
	f.p.	10^{-6}	t	440	10^{-5}	[99]
	f.p.	10^{-6}	ee	480—520	0.2	[133]
	l.p.	10^{-9}	t	420	10^{-8}; 10^{-6}	[131]
	l.p.	10^{-9}	e	440, 470	—	[131]
	l.p.	10^{-}[illegible]	pmma	470	—	[131]
SP_5	f.p.	10^{-6}	pmma	470, 530	0.2	[133, 134]
SP_6	l.p.	10^{-8}	b	440	$2\cdot10^{-7}$	[137]
	l.p.	10^{-8}	e	445	$3\cdot10^{-7}$	[137]
	l.p.	10^{-8}	an	460	$9\cdot10^{-7}$	[137]
	l.p.	10^{-9}	t, e	450	10^{-7}	[131]
SP_7	l.p.	10^{-8}	b	450	$5\cdot10^{-6}$	[135]
	l.p.	10^{-8}	ppg	450	$3\cdot10^{-5}$	[135]
	l.p.	10^{-8}	ms	450	$2\cdot10^{-6}$	[135]
SP_{16}	p.r.	10^{-8}	b	430	$2\cdot10^{-6}$	[139]
SP_{17}	l.p.	10^{-9}	t	440	10^{-6}	[97]
	l.p.	10^{-9}	an	440	10^{-8}; 10^{-5}	[97]
SP_{20}	l.p.	10^{-11}	b	440	10^{-8}	[140]
SP_{23}	l.p.	10^{-8}	b	470, 530	10^{-6}	[138]
Nitro-chromene (III)	l.p.	10^{-8}	t	330, 520	$8\cdot10^{-8}$; $4\cdot10^{-7}$	[116]

Notation: f.p. = flash photolysis, l.p. = laser photolysis, p.r. = pulse radiolysis, Δt = time resolution of the method, ch = cyclohexane, mch = methylcyclohexane, t = toluene, e = ethanol, ee = 2 : 1 ethano–ether mixture, b = benzene, an = acetonitrile, ppg = poly(propylene glycol), ms = micellar solutions, pmma = poly(methyl methacrylate).

Scheme (6) is also valid for the piperidine SP with the sole difference, that, owing to steric factors, the reaction stops at the stage involving the formation of the isomer X and not B.

The formation reaction of the coloured form of SP with the nitro-group by pulse radiolysis in benzene proceeds via mechanisms similar to that described by scheme (6) or more precisely via the "triplet channel":[55,139]

$$\begin{tikzcd} A \arrow[r, "^3C_6H_6"] & {}^3A \arrow[r] \arrow[dr] & {}^3X \arrow[r] \arrow[d, "O_2"] & A \\ & & B & \end{tikzcd} \qquad (7)$$

The lifetime of the state ^3A is $\leq 10^{-8}$ s, while that of ^3X is 2×10^{-6} s (in the absence of oxygen). The presence of atmospheric oxygen accelerates the reaction $^3X \rightarrow B$, increasing thereby the yield of B.

The influence of various quenching agents (oxygen, TMPP, and triphenylamine) on the kinetics of the decrease of the intensity of the short-lived absorption band of the SP_4 solution in toluene at 440 nm has been investigated[99] by flash photolysis using the results of a study of the quenching of the photocolouring reaction in photostationary experiments. This absorption disappeared with the rate constant $\geq 10^5$ s^{-1} and did not arise in the presence of O_2. The results obtained show that the photolysis of SP_4 proceeds via a mechanism analogous to mechanisms (6) and (7) and that the absorption band at 440 nm constitutes a superposition of the absorption bands of two SP photoproducts—^3A and ^3X.[99] Oxygen and the electron donor deactivate ^3X and ^3A respectively under these conditions.

Thus, on the basis of the results of a number of studies,[4,99,116,139,141] and taking into account the fact that in the photostationary colouring of SP with the nitro-group the reaction proceeds mainly via the triplet state, one can postulate that scheme (6) is valid for SP with the nitro-group, as for compound (III), with the sole difference that the deactivation of the ^3X state by oxygen in the case of SP leads to the formation of the B form, while in the case of compound (III) the initial form of the nitrochromene is regenerated.[116]

We shall analyse from this standpoint other studies of the photocolouring reaction by the laser flash photolysis method. The short-lived spectra of SP_3 and SP_{20} arise over a period of only $\sim 10^{-11}$ s [132,140] and the disappearance of the band at 580 and 440 nm in the initial instants proceeds in accordance with the same law with a characteristic time in the range 10^{-9}–10^{-8} s, depending on the solvent (toluene and ethanol). Hence it follows that these two bands belong to the same product. By analogy with other studies[130,137,142] and in view of the high rate of its appearance, Krysanov and Alfimov[132] assigned the 440 nm band to the $S_0 \rightarrow S_1^*$ absorption of the isomer X, assuming that it is formed from the ^1A state. Although this reaction can in fact make a definite contribution ($\lesssim 20\%$) to the formation of the isomer X and the B form,[97,116,141] nevertheless it is preferable to attribute the band to the overall absorption by the SP and the isomer X in the T states (^3A and ^3X respectively). This assignment makes it possible to explain the biexoponential kinetics of the decrease of the absorption by the short-lived products, noted in a number of investigations[132,137,140,142] and characterised by two times τ_1 and τ_2, and also the influence of the presence of oxygen on the latter. The rapid and slow components of the kinetics of the decrease of absorption can be reasonably assigned to absorption by the ^3A and ^3X states respectively. The time τ_1 for the ^3A state is then 10^{-9}–10^{-8} s, while τ_2 for the ^3X state is $\sim 10^{-7}$ s. The time τ_1 for the ^3A state agrees well with its existing estimates (see Table 4 and Refs.139, 143, 144). For such values of τ_1 and τ_2 and at a low O_2 concentration ($\sim 10^{-3}$ M), the quenching process, whose rate is determined by diffusion, can exert an appreciable influence only on the slow component of the decrease of the absorption by the short-lived products, i.e. on τ_2 for the ^3X state. Indeed it has been noted that τ_1 remains unchanged and τ_2 diminishes with the simultaneous increase of the yield of the B form in the presence of O_2.[137,139,142] The high rate of formation of ^3A is also not surprising, since K_{ST} for aromatic nitro-compounds is of the order of $\gtrsim 10^{11}$ s^{-1}. For example, the maximum intensity of the T–T absorption for nitroanisoles is attained after only $\sim 10^{-11}$ s.[76] This is also promoted by the high quantum yield (0.6–0.7) for the formation of the triplet states of aromatic nitro-compounds.[76,78,145]

Analysis of the absorption spectra of the short-lived products[131,132,140] permits the conclusion that in the case of SP, as for compounds (III), the extinction coefficients of the ^3A and ^3X states and the positions of the absorption bands are similar. In the range 570–610 nm the pattern of the variation of the short-lived spectrum may become complicated as a consequence of the superposition of the absorption band of the B form.

For SP_4 and SP_5, the assignment of the 440 nm band to the T–T absorption in PMMA [131] agrees with the results of a study[133] in which the identity of the lifetimes of the phosphorescence and of the short-lived absorption of SP_5 at 77 K was established. The character of the time variation of the spectrum of the short-lived product derived from SP_4 [131] permits the conclusion that the 420 nm band represents the superposition of the absorption bands of two products with appreciably different lifetimes—of the order of 10^{-8} and 10^{-6} s, which agrees qualitatively with the results of Kholmanskii et al.[99]

Biexponential kinetics of the decrease of the absorption at 440 nm have been observed for SP_{17} in acetonitrile;[97] the shorter-lived absorption was assigned by the authors to the S_0–S_1 absorption by the isomer X, since the decrease of the absorption intensity at 440 nm was not accpanied by an increase in the region corresponding to absorption by the B form (500–600 nm). However, as noted above, the constancy of the absorption intensity in the range 500–600 nm, which was observed also in other studies,[116,139,146] may be be due to the fact that the decrease of the ^3A absorption and hence also of the ^3X absorption is compensated by the increasing absorption by the B form.

It has been established[97] that the absorption of SP_{17} at $\lambda = 530$ nm increases with a characteristic time of 2.7×10^{-10} s (in methylcyclohexane) regardless of the initial SP concentration (the latter fact shows that the association of the SP molecules does not affect the primary photoprocesses in the molecule). This increase was attributed to the reaction $^1A \rightarrow B$ which may make a slight contribution to the formation of the B form in the case of SP with the nitro-group, as for compound (III).

Summing up the discussion of the results obtained with the aid of kinetic pulse spectroscopy, one may conclude that the formation of two products can be detected kinetically on apparatus with a time resolution $\leq 10^{-8}$ s and that the lifetime of the shorter-lived product is not appreciably influenced by oxygen. With laser pulse apparatus with a time resolution $\geq 10^{-7}$ s, a single short-lived product is detected as a rule, its lifetime depending on the presence of O_2. The identification of these products as the SP and the isomer X in the ^3A and ^3X states respectively appears to be most likely.

Thus, on the basis of the above analysis and taking into account the data in Section II and in the previous parts of the present Section, one can formulate the following general mechanism of the SP photocolouring reaction:

$$\begin{tikzcd} A \arrow[r, shift left, "h\nu"] & {}^1A^* \arrow[l, shift left] \arrow[r] \arrow[d] \arrow[drr] & {}^3A^* \arrow[r] \arrow[dr] & {}^3X^* \arrow[d] \\ & {}^1X^* \arrow[r] & X \arrow[r] & B \end{tikzcd} \quad (8)$$

The scheme does not show the recombination reaction of the excited states A^* and X^* to give A and also the transitions ${}^1X \rightarrow {}^3X$ and ${}^3X \rightarrow X$ and the reverse dark reaction $B \rightarrow A$ are entirely feasible.

The occurrence of the photocolouring reaction via a particular channel is determined by the structure of the SP and external conditions. For SP containing a nitro-group, the reaction takes place mainly via the triplet channel, while for SP without the nitro-group the singlet channel is involved. Bearing in mind that the bond dissociation reaction in the ${}^3A$ state of SP_3 has an activation barrier of 0.04 eV,[29] the photochemical reaction pathway for an SP of the type SP_3 can also be represented under these conditions by the transitions illustrated in Fig.6.

The results of the study of the kinetics of the reactions of the SP photoproducts and their lifetimes make it possible to estimate the rate constants for the transitions between them. The rate constant for the intersystem transition for SP with the nitro-group in a weakly polar solvent has values in the range $>10^{11}$ s^{-1} (transitions of the type ${}^1A \rightarrow {}^3A$ and apparently ${}^1X \rightarrow {}^3X$).[74] The rate constants for the transition ${}^3A \rightarrow {}^3X$ or B as well as the transition ${}^1A \rightarrow B$ are in the range 10^8–10^{10} s^{-1} [97] depending on the structure of the SP. The transition ${}^3X \rightarrow B(X)$ in the absence of oxygen is characterised by a rate constant of 10^5–10^7 s^{-1}. This applies to SP whose T state is photochemically active. If the T state is photochemically inactive, its lifetime increases to 10^{-6} s (SP_{22} and SP_{23}). The transitions between the isomers B, including the transition $X \rightarrow B(A)$, take place with a rate constant of ~10^7 s^{-1} at room temperature.[137] Since the transition $X \rightarrow A(B)$ can have activation barriers (Fig.6 and Refs.6 and 35), the photocolouring process can be arrested at the X-isomer formation stage as the temperature is reduced, which has in fact been observed.[35,40,73,80]

IV. PROSPECTS FOR THE EMPLOYMENT OF PHOTOCHROMIC SPIROPYRANS IN SCIENCE AND ENGINEERING

Photochromic SP have found the main application in the preparation of various recording media and in the treatment of optical information and also in the manufacture of filters with a variable optical density.[5,7,9] More than 20 light sensitive compositions of photographic materials in which SP play one role or another are patented annually in this field. Apart from their use as colour-generating components (in photochromic and free-radical photographic materials with a sensitivity up to 10^{-4} J cm^{-2},[4,147–149]), SP are also introduced as spectral sensitisers in diazotype, photopolymeric, and electrophotographic photomaterials.[7] Photochromic materials based on SP have a high resolving power (up to 10^4 mm^{-1}) and a capacity for recording and counting on a real time-scale; the light sensitivity of photochromic materials to UV light is 0.05 J cm^{-2} for a unit decrease in optical density while their sensitivity to IR irradiation is 1–2 J cm^{-2}.[4,5] The number of recording and deletion cycles on the photochromic material varies from tens to thousands depending on the optical density drop and the type of material.[5]

Photochromic materials based on SP are being improved by increasing the number of cycles which can be achieved and the light sensitivity and by creating multicolour photochromic systems and materials, which make it possible to regulate the storage time of the information recorded on them. In order to solve the latter problem, the influence of the polymer on the characteristics of the photochromic transformations and the possibility of stabilising the coloured form by selecting the appropriate polymer or the type of chemical binding of the SP to the latter are investigated[32,84,86,151–153] as is altering the structure of the SP to increase the activation barrier of the thermal decolorisation reaction.[150,151]

The light sensitivity of photographic materials based on SP, in which the image is recorded on the basis of the fluoresence of the coloured form of the SP, reaches 10^{-5} J cm^{-2}.[4,7] Materials of a similar type are nowadays being vigorously investigated and improved.

We shall consider in greater detail the use of SP as regulators of various physicochemical processes controlled with the aid of light. The principal property of SP which permits their use in this field is the sharp difference between the physicochemical characteristics of the coloured and colourless forms. The coloured form of the SP with the nitro-group is a highly polar merocyanine dye and hence it possesses the entire wide variety of properties characteristic of this class of dyes.

The possibility of the photocontrol of the potential difference on the surface of a membrane with the aid of SP has been investigated.[10,154] For this purpose, one uses the ability of the coloured form of the SP on the surface of the membrane to react effectively with a proton to form a positively charged product. The surface charge on the membrane and hence the potential difference is regulated in this way.

The possibility of using SP for the investigation of the photoregulation of ion transport through a biological membrane is extremely attractive,[154–156] particulaly the photocontrol with the aid of SP of the transport of metal salts (KCl and NaCl) and aminoacids through liquid membranes. By means of an SP, using the photochromic properties of its hydrochloride, it is possible to control the electrical conductivity of liquid solutions by means of light.[157]

The possibility of the photoregulation and investigation of the chemical reactivity of biological molecules by introducing SP into their compositions appears promising. Thus interesting studies have been made on the photocontrol of the chemical reactivity of the SP-modified α-amylase.[158–161] The mechanism of the influence of SP on the chemical reactivity of compounds is based on the change in the distribution of electron density in the molecule under the influence of the charges of the highly polar B form. The same property of the coloured form determines also the possibility of using SP as surfactants, capable of altering the surface tension at the interface between two liquids[162,163] and also of regulating with the aid of light the hydrophilicity of the polymer surface.[164–166]

The use of SP as light-sensitive additives in films and Langmuir–Blodgett monolayers is of special interest.[11,13,14,167–169] SP modified by introducing a long saturated hydrocarbon chain into the indoline or benzopyran fragment (as, for example, in SP_{18}) are used for such purposes.

Thus it is possible to modulate fluorescence by light and also to investigate the mechanism of the energy and electron transfer between layers, regulating the distance between them with the aid of intervening multilayers consisting of different numbers of monolayers but without admixtures (for example, the thickness of the cadmium arachidate layer was 25 Å [169]).

The high rates of the intermolecular reversible photochemical processes in SP (see Section III) give rise to the hope that the use of SP in multilayers of various structure in combination with the appropriate laser pulse technique will help to create interrupters or modulators of light or electric signals, which are triggered over a period of ~10^{-11} s.

Since SP exhibit photochromic properties when adsorbed on solid surfaces,[5-8] it is of undoubted interest to introduce them as light-sensitive admixtures into ordered monolayers prepared by the chemisorption of certain compounds on solid surfaces, including oriented polymers.[170-172]

The introduction of SP into liquid crystal materials and the synthesis of molecules with liquid-crystal properties on the basis of SP make it possible to expand the range of applications of the latter.[48,173-175] The preparation of photochromic compositions in the form of micellar solutions or the use of SP with amphiphilic properties makes it possible to render visible a stream of liquid to which the SP has been added[176,177] and to apply the method of flash photolysis to the study of various problems of the hydrodynamics of liquids.

It has been suggested[178,179] that SP be used as analytical reagents for the ions of a series of metals, because the latter react with the *B* form to produce intensely coloured chelate complexes.

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The 1,3-Anionic Cycloaddition Reactions of αβ-Unsaturated Thiolates and Their Analogues

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The reactions of αβ-unsaturated alkali metal thiolates and the analogous salts of selenols and tellurols involving the 1,3-anionic cycloaddition mechanism are examined. The principal factors determining the capacity of the unsaturated triad anions for 1,3-anionic cycloaddition are identified and surveyed, which makes it possible to predict the mode of the reactions of these compounds.

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I. INTRODUCTION

The reactions involving the cycloaddition of neutral 1,3-dipoles to unsaturated compounds have now been thoroughly investigated in relation to many examples. Huisgen formulated the main principles governing the structure of the 1,3-dipolar system and proposed a synchronous cycloaddition mechanism. As a result of these studies, 1,3-dipolar cycloaddition has become an important method of synthesis of heterocyclic compounds.[1]

The αβ-unsaturated compounds of sulphur and its analogues (selenium and tellurium) usually participate in 1,3-dipolar cycloaddition reactions as fairly reactive dipolarophiles and, due to the specific influence of the sulphur atom, the product is a regioisomer of the cyclic adduct different from that obtained in the case of αβ-unsaturated oxygen-containing compounds. However, the multiple bond remains the reaction site.[2]

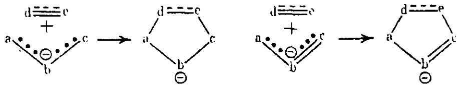
The reactions of αβ-unsaturated sulphur compounds in which they participate as 1,3-dipoles and not as dipolarophiles have also been discovered recently. Thus a group of Soviet and foreign chemists have been actively investigating the interaction of 1,2-dithiole-3-thiones, which are stable quasi-aromatic compounds, with dipolarophiles.[2,3] Drozd and co-workers extended the above reaction to allylic and propargyl derivatives of dithiocarboxylic acid esters.[4,5] In all these cases the cyclisation is accompanied by a sigmatropic shift.

Other instances of the 1,3-dipolar reactivity of sulphur compounds, for example, the adducts of carbon disulphide with phosphines or diamines, are also known.[2]

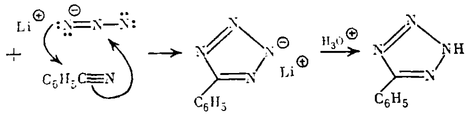
Nitrile sulphides, whose structure and reactivity are analogus to the classical 1,3-dipolar nitrile oxide systems, have been obtained recently.[6]

Thus the capacity for 1,3-dipolar cycloaddition, known previously only for oxygen and nitrogen compounds, has been recently demonstrated also for sulphur compounds.

Within the framework of the principle of the conservation of orbital symmetry in a chemical reaction, 1,3-dipolar cycloaddition is a special case of the symmetry-allowed $[_{\pi}4_s + _{\pi}2_s]$cycloaddition of allyl anions to unsaturated compounds.[7] For this reason, the allyl and propargyl anions have been used as the basis of the classification of the octet-stabilised 1,3-dipoles:[8]



The possibility of the involvement of such anions in cycloaddition reactions analogous to that of the "classical" 1,3-dipoles was predicted by Woodward and Hoffmann.[7] These reactions with participation of αβ-unsaturated anions have been called "1,3-anionic cycloaddition" (1,3-AC) on Kauffmann's suggestion.[9] The reactions involving the cycloaddition of inorganic azides (anionic 1,3-dipoles) to multiple bonds, known for a long time, can also be included among them:[1]

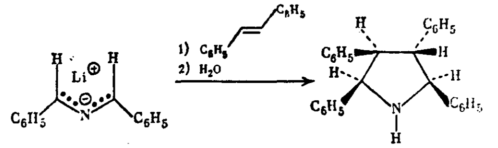


The 1,3-AC reaction of the unsubstituted allyl anion has not so far been achieved. However, allyl anions having substituents in the 2-position capable of stabilising the charge on the central atom of the triad do undergo the 1,3-AC reaction with activated alkenes. Thus 2-cyano-1,3-diphenylallyl-lithium reacts with *trans*-stilbene in a rigorously stereospecific manner with formation of the corresponding cyclopentantes. *cis*-Stilbene does not react with the salt, which confirms the concerted mechanism of the formation of new bonds.[10]

The participation of propargyl anions in 1,3-AC reactions has not been investigated, although it has been suggested that the dimerisation of 1,3-diphenylpropyne under the influence of lithium diisopropylamide proceeds via the 1,3-AC of the 1,3-diphenylpropargyl anion.[9]

The study of this key reaction, predicted by the theory, developed only after 1974 as a result of the studies by Kauffmann and co-workers devoted to the nitrogen-containing allyl anions.[9] This group of chemists demonstrated that 1,3-diphenyl-2-aza-allyl-lithium is the most reactive in 1,3-AC reactions with participation of a wide variety of unsaturated compounds ("anionophiles" according to Kauffmann's terminology).

The study of the 1,3-AC reactions of 2-aza-allyl-lithium compounds with simple alkenes demonstrated their great similarity to the reactions of 1,3-dipoles of the allylic type.[8] Thus simple unsubstituted alkenes do not react with 2-aza-allyl-lithium compounds, as in the case of the usual 1,3-dipoles. Only the introduction of phenyl substituents (styrene, stilbenes) into the dipolarophile or an increase in the strain in the multiple bond (norbornene, acenaphthylene) leads to 1,3-AC. Such reactions proceed exclusively regioselectively, as for the usual 1,3-dipoles. *trans*-Stilbene is more reactive in 1,3-AC reactions than *cis*-stilbene. In most cases the 1,3-AC proceeds stereospecifically: *trans*-stilbene reacts with *cis*-1,3-diphenyl-2-aza-allyl-lithium to form only one conformer of tetraphenylpyrrolidine:



These data indicate a concerted mechanism of 1,3-AC. Apart from the alkenes enumerated above, alkadienes and, as shown recently, arylallenes are fairly reactive in the 1,3-AC reactions with 2-aza-allyl-lithium compounds.[11] The introduction of organoelemental substituents, incorporating Group IV–VI elements in the Third and Fourth Periods such as sulphur, selenium, phosphorus, arsenic, silicon, and germanium, into alkenes favours the 1,3-AC reactions.[12]

The 1,3-AC reactions of 2-aza-allyl-lithium compounds with alkynes and nitriles frequently lead to heteroaromatic products, since they are accompanied by the elimination of hydrogen.

The nature of the multiple bond in the anionophile has a particularly pronounced influence on the 1,3-AC reactions. As in the reactions with the usual 1,3-dipoles, the oxygen-containing anionophiles are less reactive in cycloaddition to 2-aza-allyl-lithium anions than the sulphur and nitrogen compounds. Aldehydes, ketones, and carbon dioxide react with 2-aza-allyl-lithium compounds to form only linear adducts. Carbon disulphide is uniquely reactive in 1,3-AC reactions.[9]

Thus 1,3-AC reactions have been relatively thoroughly investigated only for nitrogen-containing allyl anions. The results of these studies have been summarised in a review[9] and have been included in a reference publication on general organic chemistry.[13]

Yet another type of 1,3-AC reactions involving sulphur compounds, namely αβ-unsaturated thiolates and their Group VIA analogues has been investigated in very recent years. These reactions make available new groups of sulphur-containing hereocycles and extended thereby greatly the scope of 1,3-AC in organic synthesis. The present review is devoted to a survey of the results of the authors of the review and other chemists in the study of the reactivities of αβ-unsaturated thiolates in 1,3-AC reactions.

αβ-Unsaturated thiolates are generally related to thioaldehydes, thioketones, and thioketens and the investigation of their reactivity therefore helps to extend the applications of various thiono-compounds in organic synthesis.

Ethylenic thiolates, which are salts of enethiols—a tautomeric form of thiono-compounds—have been known for a comparatively long time, while the salts of acetylenic thiols—the "enol" form of thioketens—were first obtained only in 1962.[14] The electrophilic substitution reactions of αβ-unsaturated thiolates have been most thoroughly investigated. In contrast to the enolates, which react both via the oxygen and carbon centres, unsaturated thiolates interact with electrophiles only via the thiol reaction centre.[15] Ethylenic selenolates and even more so the tellurolates were until recently difficult to obtain or were unknown owing to the instability of the initial $>C{=}Se$ and $>C{=}Te$ compounds.[16] As a result of studies mainly by Arens and his school,[14] the salts of αβ-acetylenic selenols and partly tellurols are readily available.

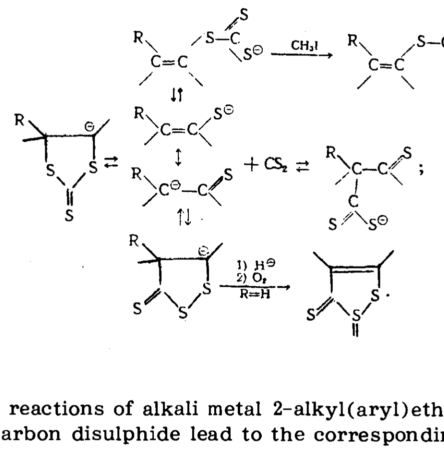
The nucleophilic character of the heteroatom in αβ-unsaturated thiolates and their analogues as well as the available data on the reactivity of 1,3-dipoles of the "allylic type"[8] have determined the choice, as objects of study, of anionophiles such as heterocumulenes and activated acetylenes, in the first place carbon disulphide, whose unique reactivity in 1,3-dipolar cycloaddition reactions is well known.[1] Furthermore, αβ-unsaturated thiolates can be successfully introduced into "mixed" dimerisation reactions with Huisgen's classical 1,3-dipoles. Such reactions have been fairly thoroughly investigated for the αβ-unsaturated compounds of tervalent phosphorus.[2] The latter are regarded as 1,3-dipolar systems with the negative charge on the phosphorus atom and the positive charge on the extreme carbon atom involved in the multiple bond.

II. INTERACTION WITH HETEROCUMULENES

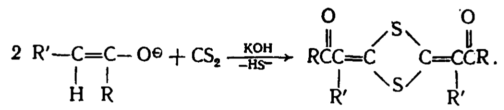
1. αβ-Ethylenic Thiolates

2-Alkyl(aryl)ethylenethiolates are usually obtained as mixtures of the *Z*- and *E*-isomers on treatment of the corresponding ethylthioethylenes with alkali metals in liquid ammonia.[17,18]

Despite the fact that carbon disulphide exhibits a unique reactivity in both 1,3-dipolar cycloaddition and 1,3-AC reactions, 2-alkyl(aryl)ethylenethiolates enter into the 1,3-AC reaction with the above anionophile with difficulty. The formation of cyclic adducts is not then the only reaction pathway. The unsubstituted ethylenethiolate does not form cyclic adducts with carbon disulphide, like the allyl anion:[19,20]



The reactions of alkali metal 2-alkyl(aryl)ethylenethiolates with carbon disulphide lead to the corresponding 1,2-dithiole-3-thione in a low yield after neutralisation and oxidation with atmospheric oxygen. The addition is preferentially to the thiol reaction centre. Treatment of the reaction mixture with methyl iodide results in the formation of methylalk-1-enyl trithiocarbonates. On the other hand, when iodine is added to the reaction mixture as the oxidant, only dialk-1-enyl disulphide is obtained.[20] In contrast to the thiolate anions, the enolate anions react with carbon disulphide to form *C*-adducts and not cyclic adducts:[21]



In order to elucidate the causes of this difference between the behaviour of enolates and αβ-unsaturated thiolates in the reaction with carbon disulphide, the charge distribution in the C(2)=C(1)–X (X = S or O) systems was estimated from ^{13}C NMR spectra and from quantum-chemical calculations.[22] It was established that the maximum negative charge is located in both cases on the heteroatom, but the nono-uniformity in charge distribution is more striking for enethiolates than enolates. In the case of enethiolates one may speak of the strong nucleophilic centre on sulphur and the weak centre on the C(2) atom, while in the enolate anion there are two nucleophilic centres of approximately equal strength [O and C(2)].

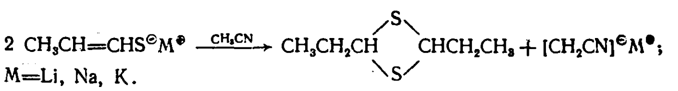
These data agree with the mode of nucleophilic addition of alkenethiolates to the electrophilic carbon atom of carbon disulphide. However, the question of the mode of addition of enolates and the mechanism of the [3 + 2]cycloaddition of alkenethiolates to carbon disulphide remains open.

The possibility that the reaction proceeds not only via the concerted mechanism but also via a stepwise mechanism is real for 1,3-AC reactions to an even greater extent than for 1,3-dipole cycloaddition.[8,9] One can assume accordingly that the reactions of an enolate with carbon disulphide belong, like the reactions of alkenethiolates, to the [$_{\pi}4_s$ + $_{\pi}2_s$] cycloaddition type, but the suggested cyclic adduct is unstable owing to the instability of the O–S bond. A similar hypothesis has been put forward in the literature for the reactions of enolates with carbonyl compounds.[23]

In order to confirm this hypothesis and to explain the causes of the observed high regioselectivity of the reaction, the results of quantum-chemical calculations for the enolate and enethiolate ions and carbon disulphide were analysed with the aid of the rules established by the molecular orbital perturbation theory in the 1,3-dipolar cycloaddition reaction.[22] Such analysis is entirely justified, since 1,3-AC also belongs to the class of [$_{\pi}4_s$ + $_{\pi}2_s$]cycloaddition reactions.

The calculations have shown that the distribution of the energy levels of the frontier orbitals in the reactions of both enethiolates and enolates with carbon disulphide belongs to Sustmann's type I. However, the estimation of the regiospecificity of the cycloaddition of enethiolates and enolates to carbon disulphide by the energy stabilisation method yields a different result for these interactions. The observed regioisomer of the cyclic anion (1,2-dithiole-3-thione and not 1,3-dithiole-2-thione) was accurately predicted in the case of enethiolates, while for the enolates the stabilisation energies of different regioisomers of the cyclic adduct are approximately the same. The reaction of the enolate with carbon disulphide is not cycloaddition. On the other hand, the same method predicts correctly the experimentally observed mode of nucleophilic addition of enethiolates and enoaltes to carbon disulphide.[22] Thus it has been suggested that the formation of 1,2-dithiole-3-thiones in the reactions of alkenethiolates with carbon disulphide proceeds via a concerted mechanism with the immediate formation of a cyclic anion and not the nucleophilic addition product, which cyclises under the influence of the oxidant after neutralisation.[20,22]

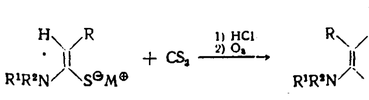
A mixture of the *Z*- and *E*-isomers of 2,4-diethyl-1,3-dithietan (the propenethiol dimer), whose formation is promoted by the presence of weak proton donors, has also been discovered in the products of the reaction of propene-1-thiolate with carbon disulphide:[19,20]



A similar dimerisation has been observed also for thioketones in the presence of bases.[24]

Heterosubstituted ethylenethiolates are much more reactive in the 1,3-AC reactions with carbon disulphide. In view of the fact that the capacity of the 1,3-dipole for cycloaddition reactions is directly related to the ability of substituents to destabilise the dipole and to stabilise the transition state,[8] the ease of the 1,3-AC should diminish in the following sequence of heteroatoms in the 1-position in the ethylenethiolate: N > O > S.

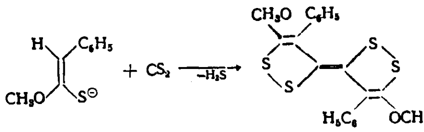
Substituted 1-aminoethylenethiolates do indeed react with carbon disulphide even at –55 °C to produce a high yield of only substituted 5-amino-1,2-dithiole-3-thiones:[25–27]



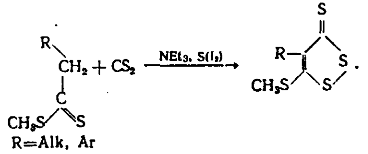
M=K, Na; R=H, Alk, Ar; R^1,R^2=Alk, Ar.

Here it is essential to note that substituted 1-aminoethylenethiolates, obtained by the reaction of thioamides with potassium or sodium amides in liquid ammonia, exist exclusively in the form of the *Z*-isomers.[28]

On the other hand, 1-methoxy-2-phenylethylenethiolate reacts with carbon disulphide only at room temperature, and more effectively on heating, the product of the oxidative dimerisation of the intermediate cyclic anion, namely 5,5'-dimethoxy-4,4'-diphenyl-1,1',2,2'-tetrathiofulvalene, being formed unexpectedly:[29]



The reactions of 1-methylthioethylenethiolates with carbon disulphide give rise to only traces of 1,2-dithiole-3-thiones. Cyclic adducts were obtained only by the reaction of the dithioesters with carbon disulphide in the presence of triethylamine and oxidants (S or I$_2$) in a solvating solvent:[25]

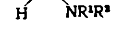


R=Alk, Ar

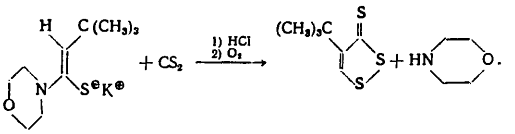
NN-Disubstituted 1-aminopropene-1-thiolates react vigorously with carbon disulphide regardless of the structure of the substituents at the nitrogen atom with formation of only the *NN*-disubstituted 5-amino-4-methyl-1,2-dithiole-3-thiones.[26]

The nature of the substituent in the β-position in *N*-substituted α-aminoethylenethiolates has a much more significant influence on the reaction with carbon disulphide.[27]

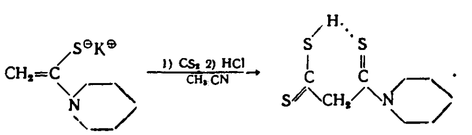
Thus, in the absence of a β-substituent, the products of the competing oxidative dimerisation, namely substituted 5,5'-diamino-1,1'-2,2'-tetrathiafulvalene, are formed apart from the usual 1,3-AC products:[27,29]



The introduction of a bulky substituent in the β-position in ethylenethiolate results in the reaction with carbon disulphide being accompanied by the elimination of an amine molecule and the formation of 4-t-butyl-1,2-dithiole-3-thione:[27]

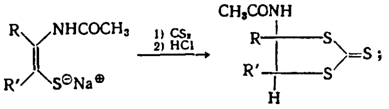


The cyclic structure of the intermediate is confirmed by the formation of a monopiperidide of trithiomalonic acid on interaction of potassium 1-piperidinoethylenethiolate with carbon disulphide in the presence of acetonitrile:



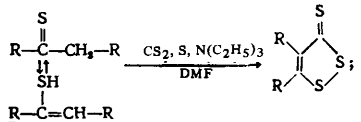
The compound isolated is not oxidised by atmospheric oxygen to the corresponding 1,2-dithiole-3-thione.[27]

Only one example of the formation of 1,3-dithiolan-2-thiones, and not 1,2-dithioles, in the reactions of alkene-1-thiolates with carbon disulphide is known in the literature, namely on interaction of 2-acetamidoethylenethiolate with carbon disulphide:[30]



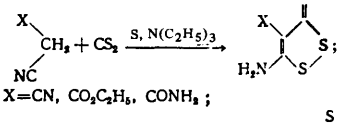
R, R'=H, CH₃

The formation of alkene-1-thiolates may be postulated as an intermediate stage in certain methods of synthesis of 1,2-dithiole-3-thiones, in the first place in the reaction of thioketones with carbon disulphide in the presence of a base (triethylamine) and an oxidant (sulphur):[24]

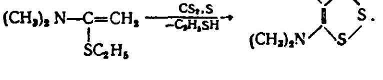


R = n-C₃H₇, iso-C₄H₉.

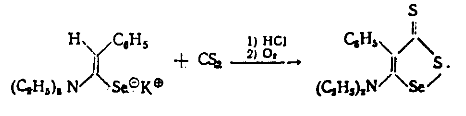
This can also occur on interaction of alkyl-substituted enamines with a mixture of sulphur and carbon disulphide[31] and also in the reactions of nitriles having mobile hydrogen atoms in the α-position with carbon disulphide and sulphur in the presence of bases[32,33] and in the exothermic reaction of keten *NS*-acetals with carbon disulphide and sulphur in dimethylformamide (DMF):[34]



X=CN, CO₂C₂H₅, CONH₂ ;



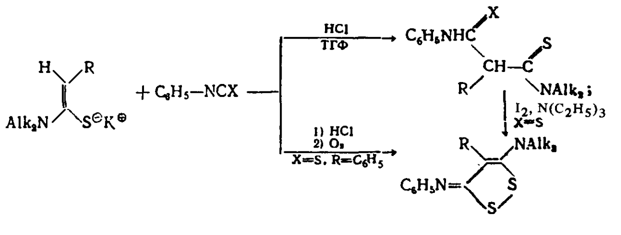
The αβ-ethylenic selenolates, which are isoelectronic analogues of alkene-1-thiolates having the amino-group in the α-position and which have been obtained recently, are also capable of entering into the 1,3-AC reaction:



The reaction is accompanied by the formation, together with a thiaselenole, also of compounds with the dithiole structure, because selenium is replaced by sulphur in the selenolate anion.[35]

Like carbon disulphide, phenyl isothiocyanate is an active dipolarophile and anionophile in 1,3-dipolar cycloaddition and 1,3-AC reactions.[1,9] In contrast to carbon disulphide, its molecule is asymmetric and, as shown in relation to the 1,3-dipolar cycloaddition reactions, it is capable of interacting via the C=S and C=N bonds.[1] However, in 1,3-AC reactions involving 2-aza-allyl anions, phenyl isothiocyanate reacts only via the C=N bonds.[9]

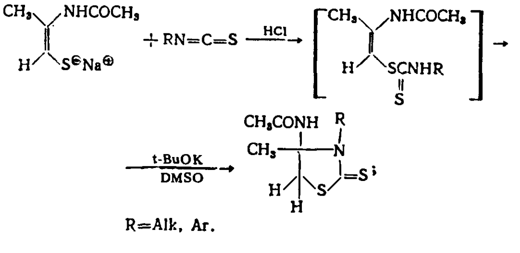
NN-Disubstituted 1-aminoethylenethiolates, which are the most reactive in the 1,3-AC reactions with carbon disulphide, combine with phenyl isothiocyanate and phenyl isocyanate via the carbon reaction centre with formation of derivatives of dithio- and mono-malonic acids respectively:[36]



R=Alk, Ar; X=O, S.

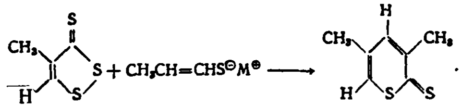
The products of the reactions of ethylenethiolates with phenyl isothiocyanates are oxidised by iodine to the corresponding 3-phenylimino-1,2-dithioles. The unusual site of nucleophilic addition (at the carbon centre of ethylene-1-thiolate) and the formation of a cyclic adduct in the reaction of 2-phenyl-1-piperidinoethylenethiolate with phenyl isothiocyanate suggest a concerted mechanism of the addition reaction. Derivatives of thiomalonic acid are formed as a consequence of the high instability of the corresponding cyclic anions. The phenyl substituent increases somewhat the stability of the cyclic anion, which is oxidised to a 1,2-dithiole after neutralisation.[28,36]

Sodium 2-acetamidoalkenethiolates react with isothiocyanates, forming, after neutralisation, linear nucleophilic addition products, which are tentatively identified as substituted dithiocarbamates. The latter cyclise to thiazolidine-2-thiones on heating in dimethyl sulphoxide (DMSO) in the presence of t-C₄H₉OK:[30]

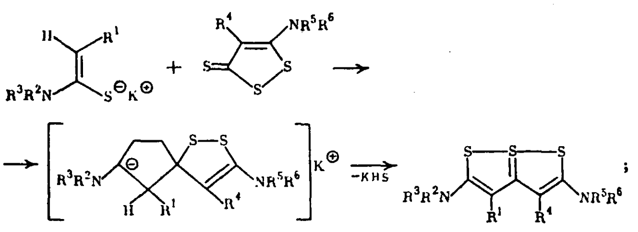


R=Alk, Ar.

Ethylenethiolates can react even with 1,2-dithiole-3-thiones. Thus the condensation of 4-methyl-1,2-dithiole-3-thione with sodium or potassium propene-1-thiolate results in the formation of 3,5-dimethylthiapyran-2-thione:[20]

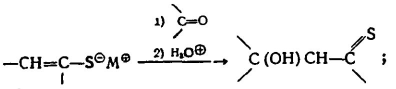


On the other hand, the interaction of *NN*-disubstituted 5-amino-1,2-dithiole-3-thiones with an excess of *NN*-disubstituted potassium 1-aminoethylenethiolate leads to derivatives of 1,6,6*a*-*S*(IV)-trithiapentalene:[37]



—R^1, R^4 = Alk, Ar, H; R^2, R^3, R^5, R^6 = Alk.

It has been shown for aza-allyl anions that the nature of the double bond involving a heteroatom has a marked influence on the 1,3-AC reaction. Thus aldehydes, ketones, and carbon dioxide react with 2-aza-allyl-lithium derivatives to form only linear products.[9] Alkene-1-thiolates react analogously with carbonyl compounds:[38-40]



$$-CH{=}\underset{|}{C}{-}S^{\ominus}M^{\oplus} \xrightarrow[2)\ H_3O^{\oplus}]{1)\ \gt C{=}O} \gt C(OH)CH{-}C(\!{=}S)\lt\ ;$$

$M^{\oplus}$=Li, Na, MgCl.

2. αβ-Acetylenic Thiolates

αβ-Acetylenic thiolates are isoelectronic analogues of 1,3-dipolar systems of the propargyl type such as nitrileimides, nitrileimines, and diazonium betaines.[8,41] Instead of the nitrogen atom, the role of the centre at which the charge is stabilised is assumed by the *sp*-hybridised carbon atom having a higher electronegativity than the sulphur atom.[42]

The cyclic anions formed on the 1,3-AC of αβ-acetylenic thiolates are more stable than in the case of αβ-ethylenic thiolates, since they have the character of the cyclopentenyl and cyclopentadienyl anions.[43] However, both the cyclopentadienyl anion and its hetero-analogues readily undergo cycloelimination for an "inexplicable" reason (in Huisgen's words[41]). Probably, the 1,3-AC reactions of αβ-acetylenic thiolates can take place only in the presence of stabilising substituents such as aromatic groups. The activating influence of such substituents has been noted for 2-aza-allyl anions[9] and for αβ-ethylenic thiolates.[19,20,25,27]

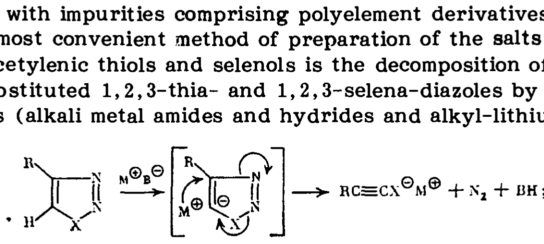
αβ-Acetylenic thiols and their analogues are unknown and are believed to be extremely unstable.[44] In the form of alkali metal salts, they are nevertheless readily available. The method of synthesis of αβ-acetylenic thiolates, selenolates, and tellurolates on interaction of acetylides with chalcogens in liquid ammonia was proposed as early as 1962:[45]

$$RC{\equiv}C^{\ominus}Na^{\oplus} + X_8 \rightarrow RC{\equiv}CXX_7^{\ominus}Na^{\oplus};$$

$$RC{\equiv}CXX_7^{\ominus}Na^{\oplus} + RC{\equiv}C^{\ominus}Na^{\oplus} \rightarrow RC{\equiv}CX^{\ominus}Na^{\oplus} + RC{\equiv}CXX_6^{\ominus}Na^{\oplus}\ \ldots\ \text{etc.};$$

R=Alk, Ar; X=S, Se, Te.

The main deficiency of this method is the synthesis of salts with impurities comprising polyelement derivatives. The most convenient method of preparation of the salts of αβ-acetylenic thiols and selenols is the decomposition of 4-substituted 1,2,3-thia- and 1,2,3-selena-diazoles by strong bases (alkali metal amides and hydrides and alkyl-lithium):[46-49]

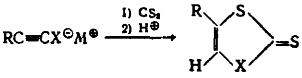


X = S, Se; R = Alk, Ar.

There also exists a convenient preparative version of the method of synthesis of an important group of thiolates and selenolates—potassium 2-arylethylenethiolates and 2-arylethyleneselenolates—by treating the corresponding thia- and selena-diazoles with KOH.[49,50]

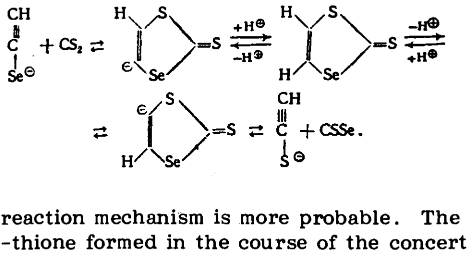
The synthesis of potassium 2-phenylethylenethiolates and 2-phenylethyleneselenolates in a pure form made it possible to investigate them by infrared and ^{13}C NMR spectroscopy. Analysis of the spectroscopic data and the results of quantum-chemical calculations demonstrated a significant non-uniformity in the charge distribution in the C≡C–X (X = S or Se) system. In the selenolate anion, this non-uniformity is more pronounced than in the thiolate anion.[51] The presence of a strong nucleophilic centre at the heteroatom in the molecules of αβ-acetylenic thiolates and selenolates agrees well with the mode of the alkylation and acylation reactions.[44,51] The non-uniformity in the charge distribution in these anions predetermines the possibility of their involvement in 1,3-AC reactions.

Compared with αβ-ethylenic thiolates, their acetylenic analogues react more vigorously with heterocumulenes containing the C=S bonds. Thus it has been established that both αβ-acetylenic thiolates[52-57] and the analogous selenolates[49,57-60] interact with carbon disulphide to form only 1,3-dithiole-2-thiones and 1,3-thiaselenole-2-thiones respectively:



M=Na, K; X=S, Se; R=H, Alk, Ar.

Some workers suggested an unusual nucleophilic addition mechanism for this reaction (the formation of a salt of trithiocarbonic acid) with subsequent intermolecular addition of the anion to the triple bond.[52] A similar reaction mechanism has been invoked to account for the results of the interaction of sodium acetylide in succession with selenium and carbon disulphide; in addition to the expected 1,3-thiaselenole-2-thione, 1,3-dithiole-2-thione, 1,3-dithiole-2-selenone, 1,3-thiaselenole-2-selenone, and 1,3-diselenole-2-thione are also formed:[60]

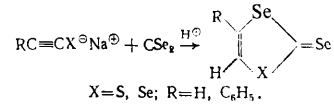


Anothe reaction mechanism is more probable. The 1,3-thiaselenole-2-thione formed in the course of the concerted 1,3-AC of ethyleneselenolate to carbon disulphide undergoes 1,3-anionic cycloelimination[61] to form ethylenthiolate and CSSe. The latter reacts further analogously to carbon disulphide.

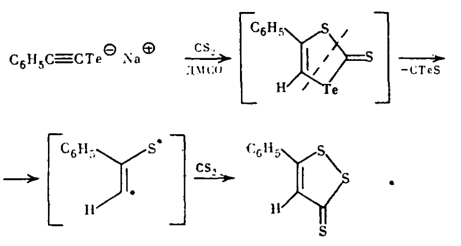
The introduction of substituents increasing the stability of the cyclic anion prevents the 1,3-anionic cycloelimination. For this reason, only 5-aryl-1,3-thiaselenole-2-thiones are formed in the 1,3-AC of 2-arylethyleneselenolates to carbon disulphide.[49,50]

The influence of substituents on the 1,3-AC has been investigated by the method of competing reactions in relation to the interaction of potassium 2-(*p*-R-phenyl)ethyleneselenolates with carbon disulphide. It has been observed that the introduction of electron-donating substituents promotes and that of the electron-accepting substituents hinders cycloaddition. As was to be expected, electron-accepting substituents stabilise the heteropropargyl system C≡CSe, while electron-donating substituents actually destabilise it.[49]

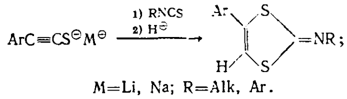
Acetylenic thiolates and their analogues react analogously also with CSe_2:[60,62]



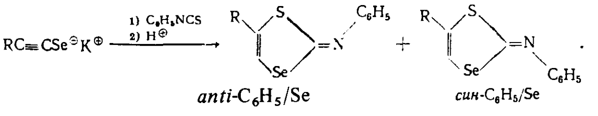
The interaction of sodium 2-phenylethylenetellurolate with carbon disulphide leads to the formation of 5-phenyl-1,2-dithiole-3-thione, which confirms the intial formation of 5-phenyl-1,3-thiatellurole-2-thione. 5-Phenyl-1,2-dithiole-3-thione could have been formed only from its decomposition products by interaction with a new carbon disulphide molecule:[63]



In contrast to αβ-ethylenic thiolates, the 1,3-AC reactions of αβ-acetylenic thiolates with isothiocyanates lead only to *N*-substituted 4-aryl-1,3-dithiole-2-imines:[64,65]

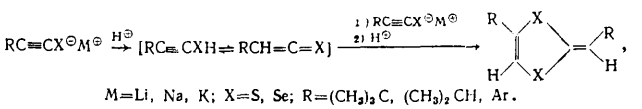


On reaction with phenyl isothiocyanate, potassium 2-aryl-(alkyl)ethyleneselenolates produce 5-aryl)alkyl)-1,3-thiaselenole-2-phenylimines in the form of mixtures of the *syn*- and *anti*-isomers, differing in the position of the benzene ring at the nitrogen atom relative to the selenium atom, in 60–80% yield:[49,64,66]

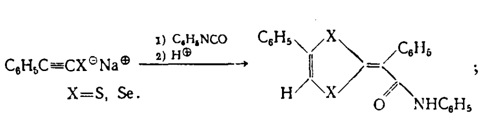


In the case of aryl-substituted selenolates, the *anti*-isomers are formed as the main product, while alkyl-substituted selenolates give rise to the *syn*-isomers.[49]

In the absence of heterocumulenes and when proton donors with pK_a < 18 (water, methanol, acids) are used, αβ-acetylenic thiolates and selenolates "dimerise" to *cis*-2,ω-diaryl-(alkyl-1,4-dithiafulvenes or their selenium analogues:[53,57,67–69]

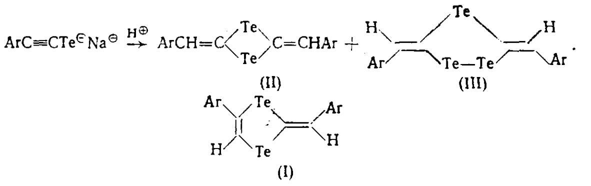


The stereoslectivity of this reaction[68,69] and its kinetics[70] confirm the occurrence of the concerted 1,3-AC of 2-aryl-substituted ethylenethiolates and ethyleneselenolates to the thio- or seleno-ketens formed from them as intermediates. This mechanism has also been confirmed by the unusual character of the interaction of sodium 2-phenylethylenethiolate or 2-phenylethyleneselenolate with phenyl isocyanate:[64]



The formation of "1,4-dichalcogenfulvenes" agrees well with the much greater reactivity of thiono-compounds compared with carbon compounds in 1,3-AC and 1,3-dipolar cycloaddition reactions.[1,9]

When the salts of 2-arylethylenetellurol are neutralised with an ethereal solution of HCl in DMSO and other similar solvents, they give rise to mixtures of *cis*- and *trans*-2,4-diarylidene-1,3-ditelluretans (II) in a satisfactory yield[63,71] and not to ditellurafulvenes (I), as expected by analogy with sulphur and selenium compounds:

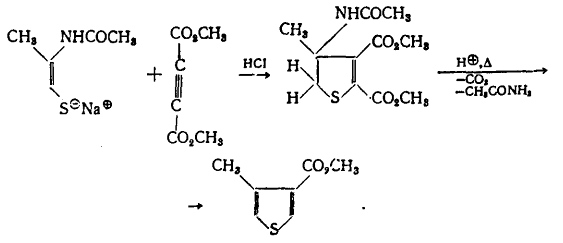


cis-3,5-Dibenzylidene-1,2,4-tritellurole (III) was isolated in an insignificant yield as an impurity.[72] The neutralisation of tellurolates with trifluoroacetic acid nevertheless leads to ditellurafulvenes (I).[73] The role of DMSO is extremely significant.[63] When diethyl ether is incompletely replaced by DMSO,[71–73] the yield of 1,3-ditelluretan (II) falls sharply.

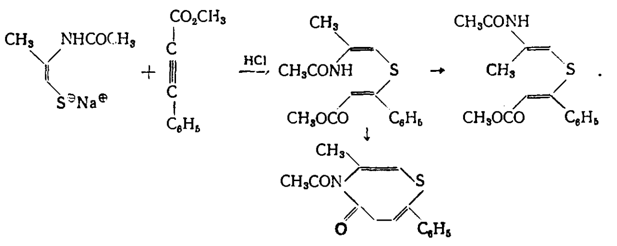
III. INTERACTION WITH ACETYLENIC COMPOUNDS

Like heterocumulenes, acetylenecarboxylate esters are active electron-accepting dipolarophiles or anionophiles in 1,3-dipolar cycloaddition or 1,3-AC reactions.[1,9] However, it has been shown that, under the conditions of the reaction of *N*-substituted 1-aminoethylenethiolates with acetylenecarboxylate esters, the latter polymerise readily.[74]

On the other hand, the interaction of sodium 2-acetamidopropene-1-thiolate with dimethyl acetylenedicarboxylate leads to a high yield of the cyclic [3 + 2]adduct—the dimethyl ester of 2-acetamido-4-methyl-4,5-dihydrothiophen-2,3-dicarboxylic acid and the product of its further reaction—methyl 4-methylthiophen-3-carboxylate:[75]

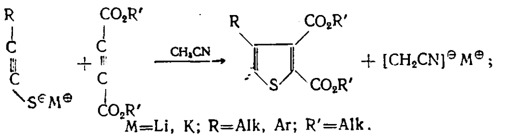


The study of the interaction of 2-acetamidopropene-1-thiolate with other anionophiles containing a triple bond (methyl ester or nitrile of phenylpropiolic acid) showed that only linear adducts—substituted divinyl sulphides—and also the products of their subsequent reaction are formed in both cases,[74] for example:



In contrast to αβ-ethylenic thiolates, the 1,3-AC reactions of αβ-acetylenic thiolates with a triple bond are energetically more favourable, since the charge redistribution takes place more readily: a more stable cyclic anion with a thiophen structure is formed.

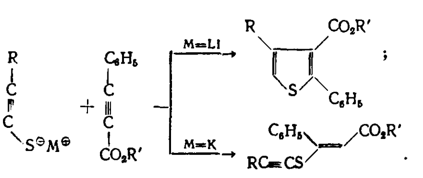
Thus it has been established that αβ-acetylenic thiolates react with acetylenedicarboxylate esters via the [3 + 2]-cycloaddition mechanism with formation of derivatives of thiophen-2,3-dicarboxylic acid:[50,67]



M=Li, K; R=Alk, Ar; R′=Alk.

The reaction proceeds most effectively in aprotic non-polar or weakly polar solvents (benzene, THF) in the presence of proton donors with pK_a = 20–25 (acetone, acetonitrile). Under these conditions, a solution of potassium 2-phenylethylenethiolate in a mixture of THF and acetonitrile contains only ion pairs, which has been demonstrated by the study of the electrical conductivities of these solutions.[77] The role of the solvents as the proton donor for the cyclic anion has been confirmed by carrying out the reaction of potassium 2-phenylethylenethiolate with dimethyl acetylenedicarboxylate in the presence of deuterioacetone. This resulted in the formation of dimethyl 4-phenyl-5-deuteriothiophen-2,3-dicarboxylate. When the reaction is carried out without a proton donor, or with proton donors having $pK_a < 18$, or in the presence of the "mild" proton donor $(CH_3)_3CBr$, the "dimerisation" of acetylenethiols to *cis*-2,ω-diaryl-1,4-dithiafulvenes takes place instead of cyclisation.[50]

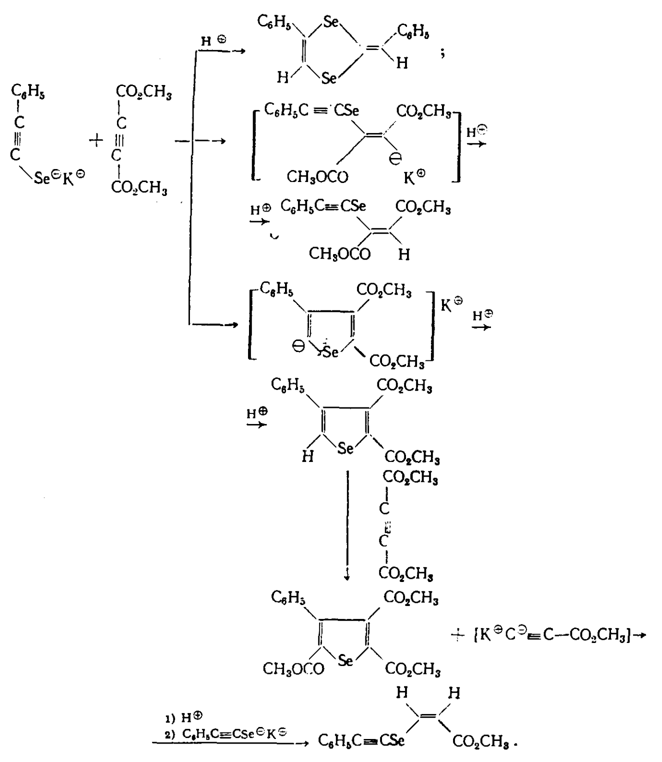
The study of the interaction of 2-arylethylenethiolates with asymmetric dipolarophiles—phenylpropiolic acid—demonstrated a significant dependence of the mode of reaction on the nature of the cation. Thus only one of the possible regioisomers of the cyclic adduct, namely alkyl 4-aryl-2-phenylthiophen-3-carboxylate, is formed in 65–82% yield from lithium 2-arylethylenethiolates. Under the same conditions, potassium 2-arylethylenethiolates gives rise to the *E*-isomers of the products of nucleophilic addition to the triple bond in phenylpropiolate esters and not to cyclic adducts:[78]



The absence of products of nucleophilic addition to acetylenedicarboxylate esters can be accounted for by the more effective stabilisation of the cyclic anion under the influence of two carboxy-groups.

In order to investigate the reactivity of acetylenic selenolates in 1,3-AC reactions wth acetylenic compounds and to determine the influence of the nature of the heteroatom, a study was made of the reactions of 2-phenylethyleneselenolate with an active anionophile—dimethyl acetylenedicarboxylate:[79]

Scheme



Careful analysis of the reaction products revealed the presence, together with the usual 1,3-AC products, namely dimethyl 4-phenylselenophen-2,3-dicarboxylate,[80,81] also of the nucleophilic addition product, i.e. dimethyl *Z*-(2-phenylethynylseleno)butenedioate, and trimethyl 4-phenylselenophen-2,3,5-tricarboxylate. The formation of derivatives of selenophentricarboxylic acid can be regarded as the result of the carboxymethylation of the selenophen anion by dimethyl acetylenedicarboxylate. The resulting methyl propiolate combines with the initial selenolate to form the ester of *Z*-3-(2-phenylethynylseleno)propenoic acid. As usual, 2,ω-diphenyl-1,4-diselenafulvene is formed as a side product.[53] The formation of these reaction products supports the intermediate existence of the anion of the substituted selenophen formed in the course of the concerted 1,3-AC reaction.

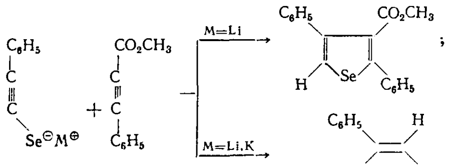
On passing from acetylenic thiolates to selenolates, the negative charge on the heteroatom increases,[51] which should promote nucleophilic addition to the heteroanion. Indeed, the products of nucleophilic addition to the triple bond of the ester were not detected in the reactions of acetylenic thiolates with dimethyl acetylenedicarboxylate.[50] Acetylenic selenolates give rise to small amounts of nucleophilic addition products, but 1,3-AC products are mainly produced.[79]

In order to investigate the influence of the cation on the selectivity of the 1,3-AC reactions of acetylenic selenolates, a study was made of the interaction of lithium 2-phenylethyleneselenolate with the same anionophile—the ester of acetylenedicarboxylic acid. The nucleophilic addition product was not then detected, the 1,3-AC product being formed with a significant increase of the yeild of the dimerisation product.[79]

All these data suggest that the influence of the cation on the mode of the reactions of selenolates with acetylenecarboxylic acid esters is due to the different states of the selenolate in the reaction medium, i.e. the different amounts of ionic character of the selenium–methyl bond.

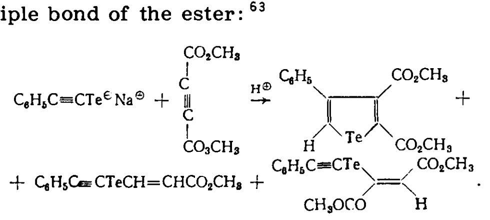
Since it is known that crown-ethers alter significantly the state of salts in solutions as a result of their coordination to the cation, the interaction of the potassium salt of 2-phenylethyleneselenol with the same anionophile was investigated in the presence of dibenzo-18-crown-6 ether. Only the cyclic adduct was then obtained in a satisfactory yield.[79]

The 1,3-dipolar cycloaddition reactions are usually highly regiospecific.[1] In order to determine the regiospecificity of the reactions investigated, a study was made of the interaction of 2-phenylethyleneselenolates with asymmetric anionophiles—phenylpropiolic acid esters.[79,82] It was then observed that the lithium salt produces only one of the possible regioisomers—methyl 2,4-diphenylselenophen-3-carboxylate, together with the product of the nucleophilic addition of the initial selenolate to the triple bond of the anionophile—methyl *Z*-3-(2-phenylethynylseleno)-3-phenylpropenoic acid:



On the other hand, the poassium salt of 2-phenylethyleneselenol (which is more nucleophilic than the lithium salt) reacts with the same anionophile to form only the nucleophilic addition product having the same *Z*-configuration.

The interaction of sodium 2-phenylethylenetellurolate with dimethyl acetylenedicarboxylate led to the dimethyl ester of 4-phenyltellurophen-2,3-dicarboxylic acid. As for selenolates, the cyclisation is accompanied by nucleophilic addition to the triple bond of the ester:[63]

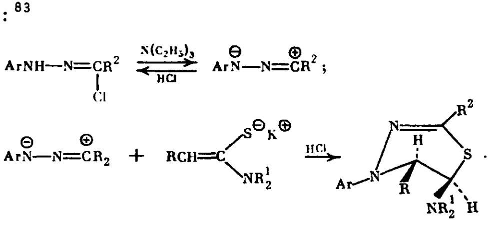


The yield of the tellurophen is appreciably lower than that of the thiophen[50] or selenophen[79] in the analogous reactions.

IV. "MIXED" DIMERISATION WITH HUISGEN'S 1,3-DIPOLES

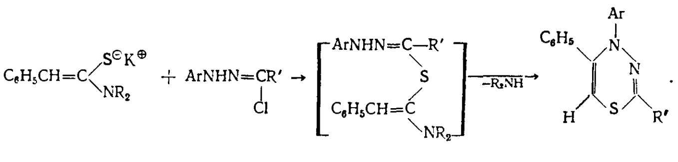
Ethylenethiolates enter into "mixed" dimerisation reactions[2] with 1,3-dipolar systems of the kind formed when HCl is eliminated on treatment with bases.[1] The hydrochloride of the base formed in the reaction reacts as a proton donor in the neutralisation of the cyclic anion.

Thus, when the *C*-chlorohydrazone is converted by treatment with triethylamine into a nitrileimine and the latter is made to react, without being isolated, with *N*-substituted 1-aminoalkenethiolates, then [3 + 3]cycloaddition products, namely 5,6-dihydro-4*H*-1,3,4-thiadiazines, are mainly obtained:[83]



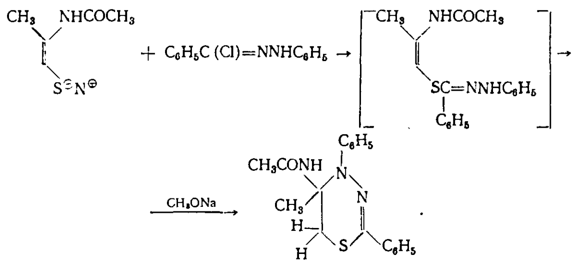
Although the formation of both "half-chair" and "half-boat" conformers with any relative disposition of the substituents is sterically feasible, nevertheless, judging from the ^1H NMR spectrum, only the "half-chair" conformer is actually formed.[83]

On the other hand, 1-*NN*-dialkylamino-2-phenylethylenethiolates react with *C*-chloro-*N*-phenylhydrazones under conditions which rule out the generation of nitrileimine, with formation of only 4*H*-1,3,4-thiadiazines,[83,84] i.e. the reaction is accompanied by the elimination of an amine:

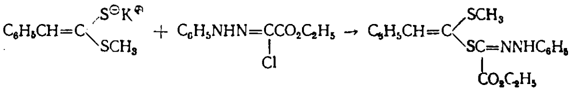


Under the reaction conditions, 5,6-dihydro-4*H*-1,3,4-thiadiazine is not converted into 4*H*-1,3,4-thiadiazine, but it does readily eliminate an amine molecule in the presence of an equimolar amount of acid or on the surface of silica gel.[83]

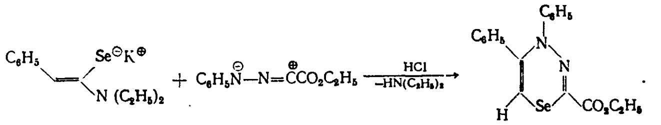
Sodium 2-acetoamidoethylenethiolate reacts with *N*-phenylmethylenehydrazonoyl chloride to form 5-acetamido-5,6-dihydro-1,3,4-thiadiazine. The product of the nucleophilic substitution of the halogen in the *C*-chlorohydrazone by the thiolate is suggested as an intermediate:[85]



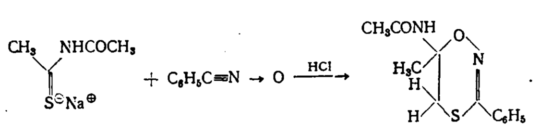
The less reactive potassium 1-methylthio-2-phenylethylenethiolate reacts with the *C*-chloro-*N*-phenylhydrazone of ethyl glyoxylate to form only the linear product of the nucleophilic substitution of chlorine:[83]



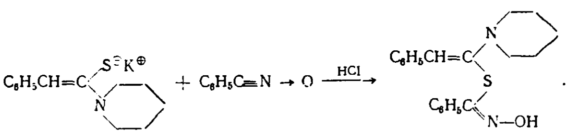
However, potassium 1-diethylamino-2-phenylethyleneselenolate readily enters into the [3 + 3]cycloaddition reaction with nitrileimines obtained from the same *C*-chlorohydrazones. forming 2-ethoxycarbonyl-4,5-diphenyl-4*H*-1,3,4-selenadiazine:[86]



Sodium 2-acetamidoethylenethiolates react also with another widely used 1,3-dipole—benzonitrile oxide,[1] forming 6-acetamido-5,6-dihydro-1,4,2-oxathiazines:

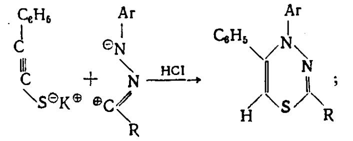


Here too it is assumed that the reaction proceeds via a two-stage mechanism.[85] On the other hand, the interaction of potassium 2-phenyl-1-piperidinoethylenethiolate with benzonitrile oxide yielded only benzohydroximoyl-2-phenyl-1-piperidinovinyl sulphide:[87]



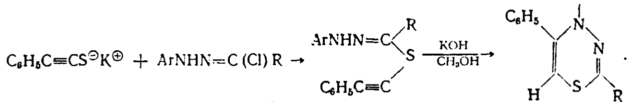
Acetylenic analogues of ethylenethiolates and ethyleneselenolates are also capable of undergoing the [3 + 3]cycloaddition reaction with the usual dipoles—nitrileimines.

Thus potassium 2-phenylacetylenethiolate reacts with nitrileimines, generated from *C*-chloro-*N*-arylhydrazones by treatment with bases, via the [3 + 3]cycloaddition mechanism with formation of 2,4,5-trisubstituted 4*H*-1,3,4-thiadiazines in a satisfactory yield:[88,89]



R=Ar, $CO_2C_2H_5$.

When the reaction of potassium 2-phenylacetylenethiolate with *C*-chloro-*N*-arylhydrazones is carried out in the absence of a base, the products of the nucleophilic substitution of the hydrogen atom—the corresponding (*C*-2-phenylethynyl sulphido)-*N*-arylhdrazones—are formed in a quantitative yield.[89] Their treatment with strong bases (KOH in methanol) results in their ready intramolecular cyclisation with quantitative formation of 4*H*-1,3,4-thiadiazines:[89]



(C-2-phenylethynyl mercapto)-N-arylhydrazones

However, under the influence of triethylamine the intramolecular cyclisation does not occur, which permits the unambiguous assumption that the interaction of 2-phenylacetylenethiolate with nitrileimine proceeds only via a two-stage mechanism.

V. CONCLUSION

Among the αβ-unsaturated heteroanions of Group VIa elements, only sulphur and selenium derivatives, in which the electronegativities of the heteroatom and the extreme C(2) atom of the anion are comparable, exhibit a distinct capacity for 1,3-AC. It has been shown for αβ-ethylenic thiolates that the introduction into the anion of substituents equalising the charge distribution and the *p*,π-electron density at C(2) and S has the greatest influence on the reactivity of unsaturated sulphur and selenium anions in cyclisation reactions.[21,28]

The influence of the heteroatom is no less significant. Thus the basicity of the heteroatom increases in the series of αβ-acetylenic thiolates, selenolates, and tellurolates, which promotes the occurrence of reactions involving the nucleophilic addition of the anion to the multiple bond of the anionophile.[50,63,79]

On the other hand, enolates have a fairly uniform charge and *p*,π-electron density distribution over the C(2) and O atoms of the triad,[21,28] but cyclic adducts are not formed. It may be that, as a consequence of the weak transmission properties of the oxygen bridge,[90] charge redistribution on formation of the cyclic anion is difficult.

The majority of the features of the 1,3-AC reactions investigated for αβ-unsaturated heteroanions can be readily accounted for from a standpoint of the concerted cycloaddition mechanism. The αβ-unsaturated heteroanions of the sulphur subgroup behave like Sustmann's type (I) 1,3-dipolar system or as electron-donating 1,3-dipoles.[21,28,51,74] The introduction of electron-donating substituents promotes and that of electron-accepting substituents hinders the 1,3-AC reactions of the anion, destabilising or stabilising its charge respectively. The stability of the intermediate cyclic anions, which increases under the influence of substituents, particularly aromatic substituents, plays an important role in 1,3-AC reactions.[40] The structure of the anionophile influences the reactivity of the unsaturated anions analogous to 1,3-dipolar cycloaddition reactions.[1] Only electron-accepting anionophiles with substituents capable of stabilising the charge give rise to stable cyclic adducts with αβ-unsaturated heteroanions.[51]

The accumulated data concerning the effect of the character and positions of substituents on the reactivity of heteropropargyl and heteroallyl anions and also the available literature data on the 1,3-AC reactions of aza-allyl anions[9] and allyl anions[10] make it possible to formulate general postulates on the basis of which a particular unsaturated triatomic anion can be assigned to systems capable of entering into 1,3-AC reactions.

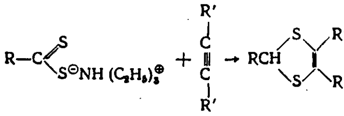
1. A uniform distribution of the *p*,π-electron density at the extreme atoms of the triad is necessary. It can be achieved either as a result of their approximately equal electronegativities or by introducing the appropriate substituents.

2. Since the reactions involving the 1,3-AC of αβ-unsaturated anions to anionophiles are accompanied by a cyclic charge shift on formation of the cyclic anion, the bonds and atoms entering into the composition of the αβ-unsaturated anions must have satisfactory transmission properties. The bonds both in the anion and in the anionophile must have high polarisabilities.

3. The cyclic anion formed as an intermediate must be stabilised either by the increased electronegativity of the central atom of the triad, or by conjugation with a substituent, or by the removal of the anionic group. Otherwise the reaction proceeds with formation of linear products of addition to the multiple bonds with retention of the same regioselectivity as in the cycloaddition.

Using these principles, it is possible to predict the reactivities in the 1,3-AC reactions of heteroallyl anions containing Group V and VI elements which have not been investigated in this respect. Thus the $R_2C{=}N{-}X^{\ominus}$ or $R{-}C\begin{smallmatrix}{\nearrow X}\\{\searrow X^{\ominus}}\end{smallmatrix}$ (X = S or Se) systems having substituents such as aryl, heteroaryl, CH=CHR, or C≡CR at the central atom should be reactive in 1,3-AC reactions.

Indeed it has been found recently that the trialkylammonium salts of aromatic and heteroaromatic dithiocarboxylic acid[91–93] interact with active anionophiles, forming the corresponding 1,3-dithioles:



R'=CO_2CH_3, CF_3.

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1,3,2-Diheterophosphacyclanes Containing a Hexacoordinate Phosphorus Atom

R.A.Cherkasov and N.A.Polezhaeva

Data are presented on the methods of synthesis, structure, and physical and chemical properties of cyclic compounds of hexacoordinate phosphorus-λ^6-1,3,2-diheterophosphacyclanes, in which the phosphorus atom is incorporated in one, two, and three heterocycles containing P-O or P-N bonds. The dynamic stereochemistry and equilibrium dissociative as well as tautomeric processes involving them are described. The role of phosphorus(VI)† intermediates in the reactions of organophosphorus compounds with tricoordinate, tetracoordinate, and pentacoordinate phosphorus is analysed. The bibliography includes 140 references.

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I. INTRODUCTION

Compounds of hexacoordinate phosphorus (phosphorates) began to be investigated vigorously only in the last decade, although the first description of substances of this type dates back to 1954 and is associated with the study of the adducts of PCl_5 with pyridine (see Dillon et al.[1,2] and the references quoted therein). Numerous inorganic "ate" complexes formed by compounds of pentacoordinate phosphorus and basic substances[3] as well as cyclic and acyclic organylhalogenophosphorates[4] are known. Cyclic phosphorates with six P–C bonds and aromatic substituents and finally λ^6-1,3,2-diheterophosphacyclanes with monocyclic, bicyclic, and tricyclic structures were later described. Individual aspects of the chemistry of compounds of hexacoordinate phosphorus have been dealt with in reviews.[5-8]

Numerous phosphorus(VI) compounds are now known and their number continues to grow, which undoubtedly indicates an appreciably greater role of these compounds in phosphorus chemistry than has been assumed hitherto. Hexacoordinate intermediates in the reactions of organophosphorus compounds containing a phosphorus atom with a lower coordination number are apparently important. Interesting data have been obtained on the steric structures of phosphorates and the equilibrium processes involving them.

Analysis of the literature data has shown that the stability of hexacoordinate phosphorus compounds increases sharply following the incorporation of the phosphorus atom in one or several rings, mainly five-membered rings. The acyclic alkoxyphosphorates known at the present time[9] are stable only in solution.

The first attempt has been made in the present review to give a systematic account of the available literature data on 1,3,2-diheterophosphoacyclanes containing a phosphorus(VI) atom entering into the composition of one, two, or three rings, mainly four- or five-membered rings, and bound to several heteroatoms (O, N). Data on the methods of synthesis, structure, physicochemical, and chemical properties of these compounds, the dynamic and equilibrium processes involving them, and the role of phosphorus(VI) compounds as intermediates in the chemical reactions of organophosphorus compounds (OPC) were used in the review.

The data on the compounds of hexacoordinate phosphorus with the 1,3,2-diheterophosphacyclane structure, summarised in the present review, supplement the available information about the reactivities of similar heterocyclic compounds containing tricoordinate,[10] tetracoordinate,[11] and pentacoordinate[12] phosphorus atoms and in our view they provide at the same time an integral picture of the chemistry of 1,3,2-diheterophosphacyclanes.

II. SYNTHESIS AND REACTIONS

Phosphorates of two types are known: those with salt (ionic) structures, in which the phosphorus atom is part of the composition of a phosphorus(VI) anion or (more rarely) a phosphorus(VI) cation, and neutral molecules, which exist in the form of dipolar ions with an anionoid phosphorus atom. A convenient analytical criterion whereby it can be demonstrated that the phosphorus atom has a coordination number of six is the marked shielding of the $^{31}P(VI)$ nucleus; it is manifested by the fact that the signals in the NMR spectra are displaced to very strong fields (between −70 and −300 p.p.m.). As already stated, the cyclisation of phosphorus(VI) compounds tends to increase their stability; the acyclic organylphosphorates $(MeO)_6P^-$ and $(EtO)_6P^-$ have been identified by ^{31}P NMR in solutions. They decompose when an attempt is made to isolate them from solution.[9]

1. Monocyclic Phosphorates

The commonest method of synthesis of monocyclic phosphorates involves the reactions of phosphorus pentahalides with bifunctional nucleophiles in which one of the halogen atoms at the pentacoordinate phosphorus is substituted and

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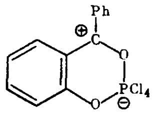
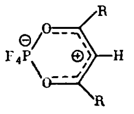
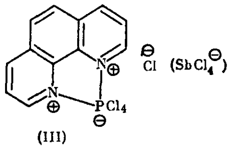
† [Roman numerals used in this way refer to coordination number and not to oxidation state in this review (Ed.of Translation)].

a sixth phosphorus–element bond is formed as a result of the donor–acceptor interaction of the electron-deficient P(V) atom with a second basic centre of the bidentate organic ligand. The reaction of *o*-hydroxybenzophenone with PCl_5 leads to a quantitative yield of the six-membered cyclic phosphorate (I), to which the structure of a dipolar ion has been attributed on the basis of the spectroscopic data and the high dipole moment (9.17 D):[13]

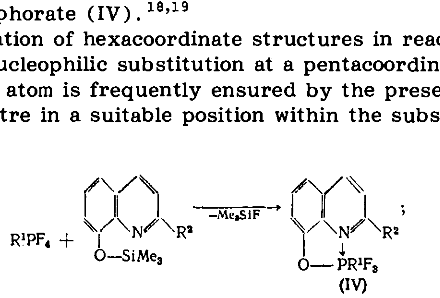

(I)


(II)


(III)

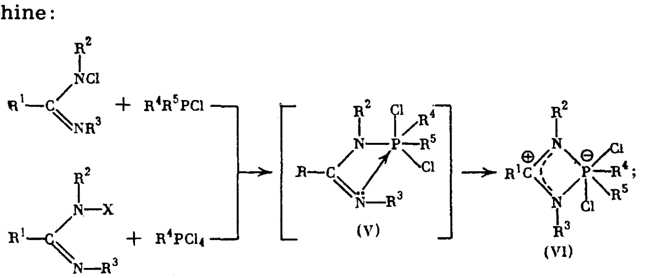
β-Dicarbonyl compounds evidently react in the enolic form, as in the formation of λ^6-1,3,2-dioxaphosphorinane (II).[14,15] Substitution by a neutral nitrogen-containing base is accompanied by the quaternisation of the donor centre [in structure(III)][16,17] and the strength of the donor–acceptor bond increases after the introduction of electron-accepting substituents at the phosphorus atom, for example, for R^1 = F in the phosphorate (IV).[18,19]

The formation of hexacoordinate structures in reactions involving nucleophilic substitution at a pentacoordinate phosphorus atom is frequently ensured by the presence of a donor centre in a suitable position within the substituting reagent:



R^1=F, Me, Et, Ph; R^2=H, Me.

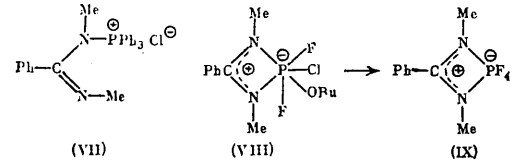
The intramolecular cyclisation of *NN'*-dialkyl-*N*-halogenophosphoranylamidines (V), formed in the reaction of *NN'*-disubstituted amidines with the chlorides of tricoordinate or pentacoordinate phosphorus made it possible to obtain a series of phosphorates (VI) containing the 1,3,2-diazaphosphetidine ring.[20–23] We may note that the reaction of *N*-chloroamidines constitutes in essence the 1,1-addition of the N–Cl fragment to the P(III) atom of the chlorophosphine:



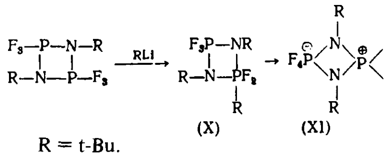
X = H, $SiMe_3$; R^1 = Ph, CCl_3, CF_3; R^2, R^3 = alkyl; R^4, R^5 = alkyl, aryl, halogen.

The reaction of *NN'*-dimethyl-*N*-trimethylsilylbenzamidine with bis(*o*-phenylenedioxy)chlorophosphorane results in the formation of tricyclic phosphorates.[20]

The stability of the four-membered monocyclic phosphorates (VI) depends greatly on the character of the substituents at the phosphorus atom and in the N–C–N triad. The benzamidinium derivative with four chlorine atoms at the phosphorus atom (VI, R^1 = Ph, R^2 = R^3 = Me, R^4 = R^5 = Cl) is the most stable. The replacement of the phenyl group at the amidinium carbon atom by the electron-accepting CCl_3 and CF_3 groups destabilises the P(VI) structure, inducing the reversible P → C migration of a chlorine atom[22] (see Section IV). An increase in the bulk of the substituent at the nitrogen atom and the introduction of two phenyl groups at the phosphorus atom lead to the same result. Three phenyl groups at the phosphorus atom stabilise only the phosphonium salt (VII),[23] while the butoxy-group induces the disproportionation of the alkoxyphosphorate (VIII) to the tetrafluoro-analogue (IX).[21]

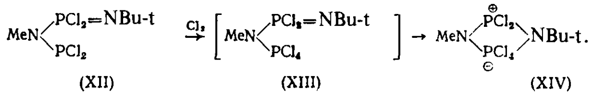


Hexacoordinate phosphorus compounds may prove to be more stable than the phosphoranes having the analogous structure. Thus the presence of bulky substituents in the diazadiphosphetidine ring induces the rearrangement of the phosphorane (X) to the corresponding phosphorate (XI):[24]

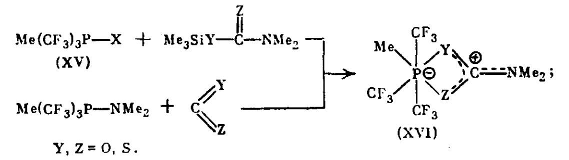


R = t-Bu.

The intramolecular addition of the nucleophilic imino-nitrogen to the P(V) atom, inducing the formation of stable phosphorates, can occur so readily that, for example, in the chlorination of the aminophosphimine (XII) the resulting phosphorane (XIII) rearranges immediately to the phosphorate (XIV):[25]



The reactions of halogenophosphoranes (XV) with silylcarbamates lead analogously to the phosphorate-carbamates (XVI) in a high yield.[26–28] The latter are also obtained when CO_2, COS, and CS_2 are inserted in the P–N bond in aminophosphoranes (XVII):

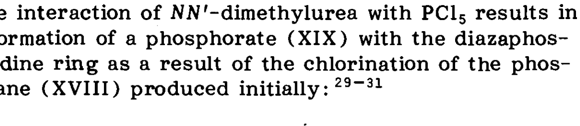


Y, Z = O, S.

The monothiocarbamates (XVI, Y = O, Z = S) are converted quantitatively into the dithio-derivatives on treatment with carbon disulphide. The resonance of the phosphorus atom in the phosphetidines (XVI) is characterised by a signal at very high field (between −251 and −298 p.p.m.).

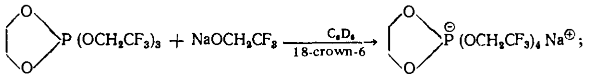
Phosphorus(VI) compounds may be formed from phosphoranes also as a result of the addition to the electrophilic P(V) atom of "external" nucleophiles—the anions of proton-containing nucleophiles and neutral *n*-donor Lewis bases.

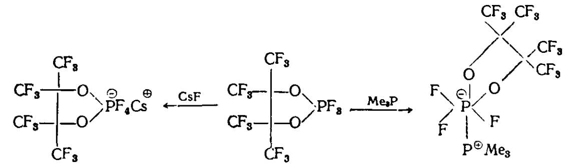
The interaction of *NN'*-dimethylurea with PCl_5 results in the formation of a phosphorate (XIX) with the diazaphosphetidine ring as a result of the chlorination of the phosphorane (XVIII) produced initially:[29-31]


(XVIII) (XIX)

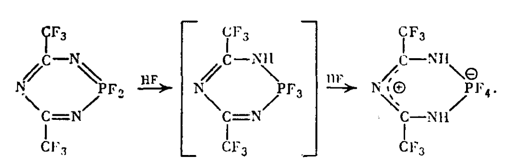
Further substitution of the chlorine atoms in compound (XIX) on treatment with dimethylurea leads to a phosphorate of the spiran type, which, however, cannot be isolated from solution.[32]

Monocyclic phosphoranes are characterised by a pronounced Lewis acidity and readily react with anions, being converted into stable phosphorates. Thus, in the presence of crown-ether, the phosphorane (XX) is converted by alkoxide into the corresponding sodium phosphorate,[33] while the perfluoropinacol trifluorophosphorane combines with both a fluoride anion and a neutral trimethylphosphine molecule, forming stable phosphorates with the characteristic chemical shifts of the P(VI) and P(IV) atoms in compound (XXI):[34,35]


(XX) $\delta(^{31}P) = -128$ p.p.m.


$\delta(^{31}P) = -122.9$ p.p.m. (XXI) $\delta(^{31}P) = -130, +20$ p.p.m.

The formation of the six-membered monocyclic phosphorate (XXIII) as a result of the addition of hydrogen fluoride to the N–P=N triad of the cyclophosphazene (XXII) has been described:


(XXII) (XXIII)

The structure of the dipolar phosphorate (XXIII) was demonstrated by the IR, ^1H, ^{19}F, and ^{31}P NMR spectra [$\delta(^{31}P) = 162.7$ p.p.m.] and mass-spectrometrically.[36]

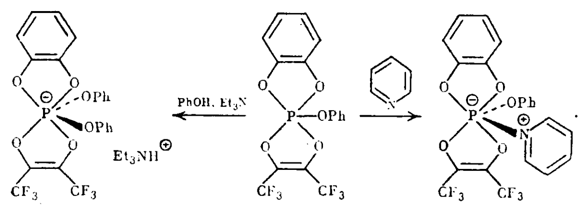
The thermal and hydrolytic stabilities of phosphorates are close to the corresponding properties of phosphoranes. Chlorine-containing phosphorates are usually very sensitive to moisture, while certain fluorine-containing compounds exhibit an appreciable hydrolytic stability.[37]

As already mentioned, the high-field position of the P(VI) signal in the ^{31}P NMR spectra, characteristic of phosphorates, can be convienently used for the identification of the latter. The values of $\delta(^{31}P)$ for monocyclic phosphorates are in the range −100–−200 p.p.m., while for acyclic P(VI) compounds the $\delta(^{31}P)$ reach −300 p.p.m.;[38,39] the phosphorus atom in fluorine-containing phosphorates usually resonates in somewhat weaker fields.[40] The shielding of the phosphorus nucleus as a rule diminishes when the P(VI) atom is incorporated in one or more five-membered rings (see Section III).

2. Bicyclic Phosphorates

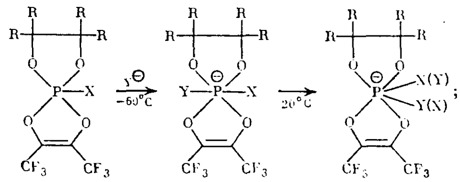
The incorporation of a phosphorus atom in one or two heterocycles is known to stabilise hypervalent structures.[12] This is equally valid also for P(VI) compounds: the stability of phosphorates increases on passing from acyclic to monocyclic and bicyclic and further to tricyclic λ^6-phosphacyclanes.

The commonest method of synthesis of bicyclic phosphorates involves the addition of ionic or neutral nucleophiles to the P(V) atom in the corresponding spirophosphoranes. The addition of the phenoxide ion or pyridine to the spirophosphorane (XXIV) leads to the spirophosphates (XXV) and (XXVI) respectively with two bidentate and two monodentate ligands:[41,42]


(XXV) (XXIV) (XXVI)

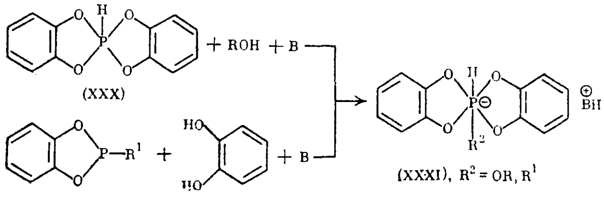
The ionic compound (XXV) is more stable than the dipolar ion (XXVI), which regenerates the initial phosphorane after prolonged heating.

The addition of ionic nucleophiles to the phosphoranes (XXVII) results in the formation of the more stable *cis*-phosphorates (XXIX), which are the products of thermodynamically controlled reactions; under the conditions of kinetic control, the *trans*-isomers (XXVIII) arise and undergo the *trans–cis* isomerisation as the temperature is increased.[41,43-48]

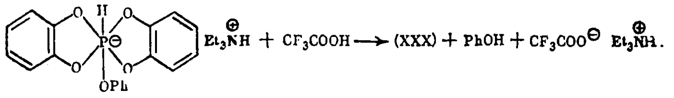

(XXVII) (XXVIII) (XXIX)

X, Y = F, OC_6H_4F-*p*.

Compounds with a P–H bond, namely hydrophosphorates, constitute an interesting group of phosphorates. They can be synthesised from the hydrophosphoranes (XXX) by treatment with alcohols in a basic medium[49-55] or by the reaction of monocyclic phosphonites with catechol under the same conditions:[49,56-60]


(XXX) (XXXI), R^2 = OR, R^1

The hydrophosphorates (XXXI, R^2 = OPh) regenerate phosphoranes in many instances on treatment with acids via a reaction which is the opposite to that of the formation reaction of the P(VI) compounds:[50]



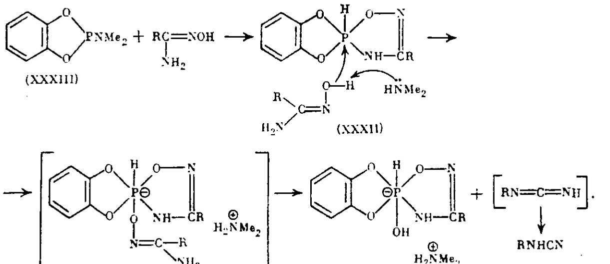
(XXXI)

Acetic acid does not induce this decomposition, i.e. the basicity of the phosphorate (XXXI) is intermediate between that of MeCOO$^-$ and CF$_3$COO$^-$.

The ease of formation of phosphoarates from spirophosphoranes and nucleophiles depends on the Lewis acidity of the P(V) atoms and increases as the cyclic substituents become more electron accepting.[54] The greatest tendency to be converted into P(VI) compounds is shown by spirophosphoranes containing 4,5-benzo-1,3,2-dioxaphospholan rings; spirophosphoranes with alkylenedioxy-substituents do not form hydrophosphorates on interaction with alcohols.[55]

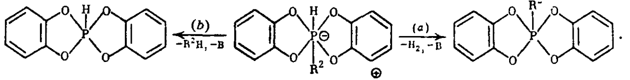
The spirophosphoranes (XXXII), which are derivatives of catechol and amidoximes, are sufficiently electrophilic to combine with the protic nucleophiles methanol, aminoalcohols, and amidoximes in non-polar solvents in the presence of bases, although the interaction with pyridine has not been observed under these conditions.[53] In polar solvents, phosphorates decompose to symmetrical phosphoranes.

The interaction of the phospholan (XXXIII) with amidoxime in solution in the benzene–ether mixture takes place in an unusual manner. Substitution of the dimethyl amino-group and subsequent reaction of the phosphorane (XXXII) with amidoxime proceed via the hydrophosphorate (XXXIV) stage, in which the N–O bond is broken. This leads to the phosphorate (XXXV), containing the P–OH and P–H groups, the first of the hydroxyphosphorates described:[53]



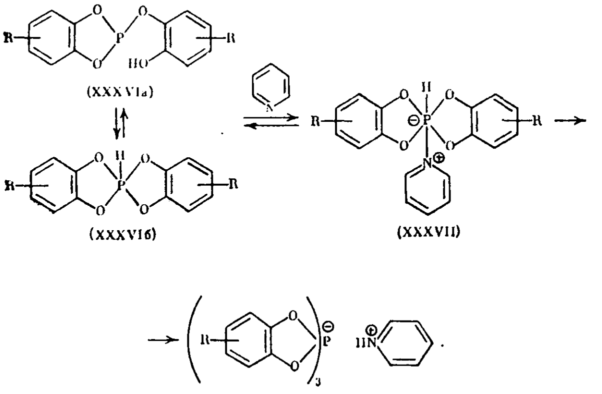
(XXXIII) (XXXII) (XXXIV)

At elevated temperatures, the hydrophosphorates (XXXI, B = Et$_3$N) decompose. The decomposition pathway depends on the nature of the exocyclic substituent R^2: for R^2 = Me, t-Bu, or Ph, hydrogen is evolved and alkyl(phenyl)spirophosphoranes are obtained (pathway *a*). The presence at the phosphorus atom of groups which can be eliminated more readily (R^2 = Ph or OMe) results in the regeneration of the amine and the hydrophosphorane (XXX) (pathway *b*):[56–60]



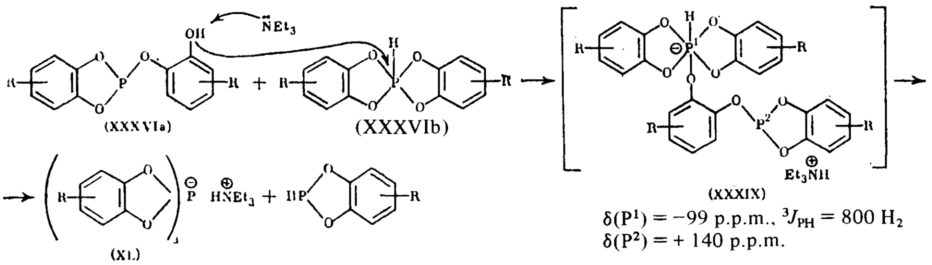
(XXX) (XXXI)

On dissolution in pyridine, the spirophosphoranes (XXXVI) interact with the solvent. The dynamics of this process has been investigated (see Section VI) and the very hygroscopic phosphorate (XXXVII) has been isolated.[42,61–63] In the course of 24 h, it is converted into the tricyclic phosphorate (XXXVIII):



(XXXVIa) (XXXVIb) (XXXVII) (XXXVIII)

In the presence of stronger bases (triethylamine, triethylenediamine, and di-isopropylamine), the reaction does not stop at the hydrophosphorate stage and a tricyclic phosphorate is formed immediately. It has been suggested[63] that stronger (harder) bases react with the tautomeric P(III) form of the hydrophosphorate (XXXVIa), which gives rise, with participation of the hydrophosphorane (XXXVIb) to the phosphite-phosphorate (XXXIX) and subsequently the phosphorate (XL):



(XXXVIa) (XXXVIb) (XXXIX) (XL)

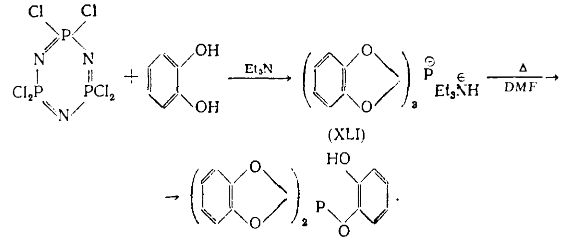
δ(P^1) = −99 p.p.m., $^3J_{PH}$ = 800 H$_2$
δ(P^2) = + 140 p.p.m.

An analogous process probably occurs also in the case of spirophosphoranes with a P–OH bond.[64]

3. Tricyclic Phosphorates

Among all the derivatives of hexacoordinate phosphorus known at the present time, tricyclic phosphorates together with halogenophosphorates constitute the most numerous group of compounds. The inclusion of the P(VI) atom in the octahedral structure of the spirotricyclophosphorate, especially one made up of three five-membered rings, increases sharply its thermodynamic stability (reduces the molecular energy). It is therefore not surprising that tricyclic phosphorates have been some of the first organic compounds with a hexacoordinate phosphorus atom to be synthesised and characterised.

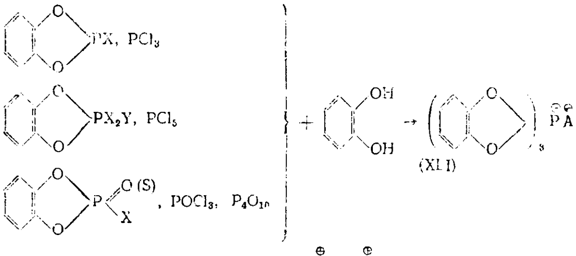
The first tricyclophosphorate was obtained as a result of the unexpected and interesting reaction of hexachlorocyclotriphosphazene with catechol in the presence of triethylamine.[65–70] *o*-Aminophenol reacts analogously:


(XLI)

(XLII)

After the phosphorate (XLI) has been heated for a long time in anhydrous dimethylformamide (DMF), the phosphorate (XLII) is formed, while in the presence of moisture the product is tri(*o*-phenyl) phosphate. The latter is also obtained on hydrolysis of compound (XLI) with hot water and on acidolysis with inorganic acids.

The thermodynamic ease of formation of the tris(phenylenedioxy)phosphorate anion determines the course of many reactions of compounds of tricoordinate, tetracoordinate, and pentacoordinate phosphorus with catechol in the presence of bases[12,71–74] or with the dilithium salt of catechol:[75]

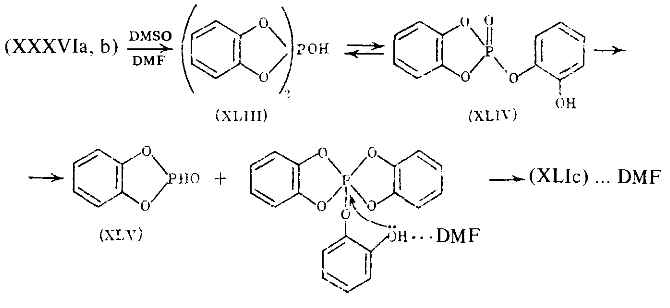

(XLI)

X, Y = halogen $\overset{\oplus}{A}$ = $Et_3\overset{\oplus}{N}H$ (a), Me_2NH_2 (b), H (c)

2,2′-Dihydroxybiphenyl reacts with PCl_5 to form a phosphorate with three seven-membered rings.[74]

The phosphorate (XLIc) is stable only in a basic medium (DMF, DMSO, amines) and apparently exists in solutions in the form of the free acid;[71] it has been suggested[64] that in weakly basic solvents this compound exists in the tautomeric P(V) form (XLII).

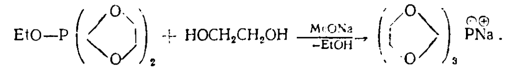
The tricyclophosphorate of type (XLIc) is formed as a result of the oxidation of the hydrophosphoranes (XXXVIa, b) with DMSO, sulphur, or iodine in DMF. The reaction evidently takes place via a stage involving the hydroxyphosphorane (XLIII), which interacts with its tautomeric phosphate form (XLIV), and is completed by the formation of the phosphite (XLV) and the phosphorates (XLIc) bound in a hydrogen-bonded complex with a solvent molecule:[64]


(XLIII) (XLIV)

(XLV)

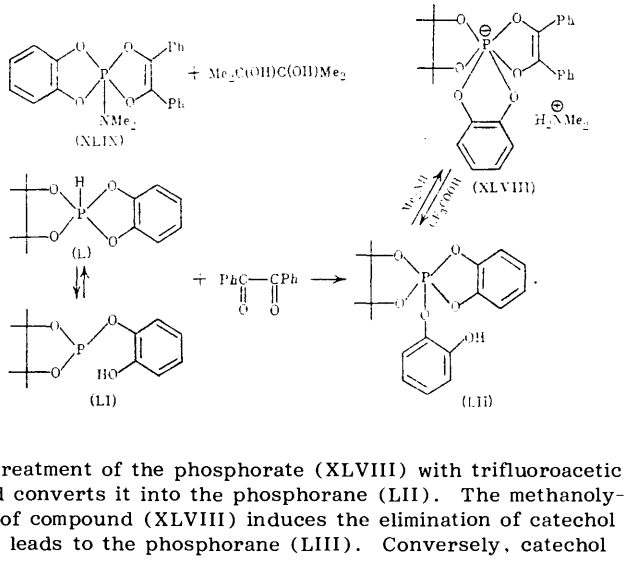
Reactions involving the substitution of mobile ligands in phosphoranes by bifunctional compounds and reactions in which bidentate ligands add to tervalent phosphorus compounds have been fruitful for the purpose of the synthesis of phosphoranes.

The first of these principles constituted the basis of the synthesis of the aliphatic tricyclic phosphorate (XLVII) by the reaction of ethylene glycol with the spirophosphorane (XLVI):[76]


(XLVI) (XLVII)

Compound (XLVII) does not melt before decomposition (300–310 °C). The attempts to obtain other aliphatic tricyclophosphoranes by this method were unsuccessful.

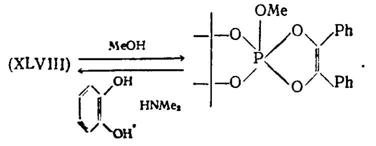
The phosphorate (XLVIII), made up of three different rings, arises analogously when the exocyclic dimethylamino-group in the spirophosphorane (XLIX) is substituted by a diol. The same λ^6-phosphacyclane (XLVIII) can be arrived at using the interaction of the hydrophosphorane (L) [which is apparently involved in the reaction in its tautomeric phosphite form (LI)] with benzil in the presence of dimethylamine:[77–82]


(XLIX) (XLVIII)

(L)

(LI) (LII)

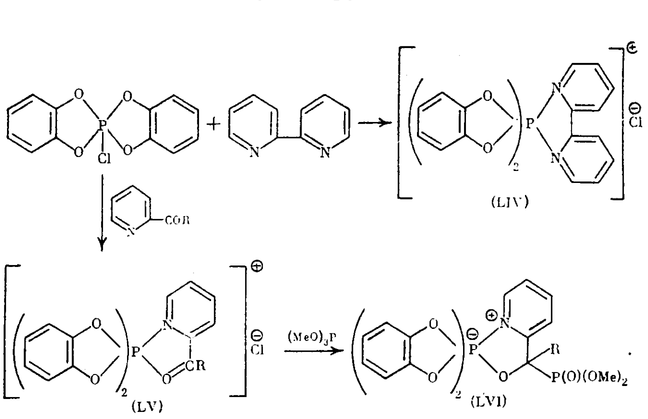
Treatment of the phosphorate (XLVIII) with trifluoroacetic acid converts it into the phosphorane (LII). The methanolysis of compound (XLVIII) induces the elimination of catechol and leads to the phosphorane (LIII). Conversely, catechol and dimethylamine readily convert the methoxyphospha(V)-cyclane (LIII) into the phosphorate (XLVIII) at room temperature:[78,81]



(LIII)

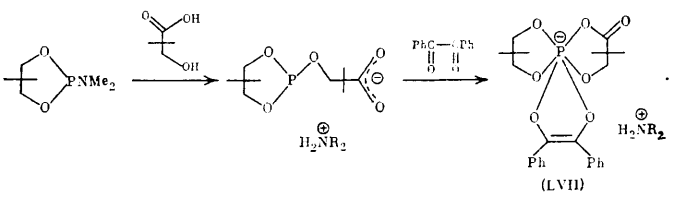
These reactions reflect the comparative ease of the interconversions P(V) ⇌ P(VI) in the presence of acids and bases (see Section IV).

Substitution with subsequent intramolecular cyclisation via the formation of the N → P donor–acceptor bond made it possible to synthesise cationic compounds with hexacoordinate phosphorus from bipyridyl and pyridyl ketone:[43,83,84]



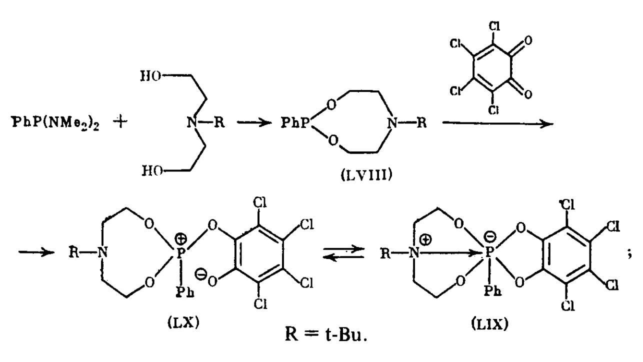
The anion exchange of the chlorine in the phosphorate (LIV) makes it possible to obtain other P(VI) compounds, including an exotic molecule in which the hexacoordinate phosphorus is present in both the anionic and cationic components.[43] The phosphorate (LV) enters into the Arbuzov reaction, forming the phosphonato-phosphorate (LVI) in the form of two spectroscopically different diastereoisomers[84] (see below).

The second principle governing the increase of the coordination number of the phosphorus atom to six with formation of tricyclic phosphorates involves the addition of bifunctional nucleophiles to the phosphorus atom in cyclic phosphites having in the exocyclic substituent a group capable of adding to the phosphorus centre.[85] Thus the reactions of cyclic phosphoramidites with hydroxy acids and further with α-diketones lead to the tricyclophosphorates (LVII):



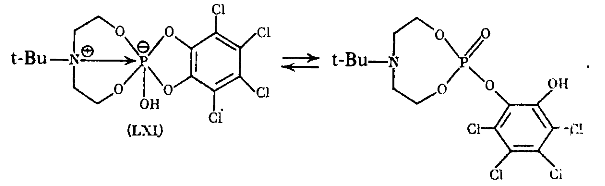
(LVII)

The phosphite (LI) is converted analogously into the phosphorate (XLVIII), while 1,3,6,2-dioxazaphosphocane (LVIII), obtained from a phosphonamidite and *N*-t-butyldiethanolamine, reacts with chloranil to form the phosphorate (LIX), in which the coordination number of phosphorus, equal to six, is determined by the formation of the transannular N → P bond:[86]



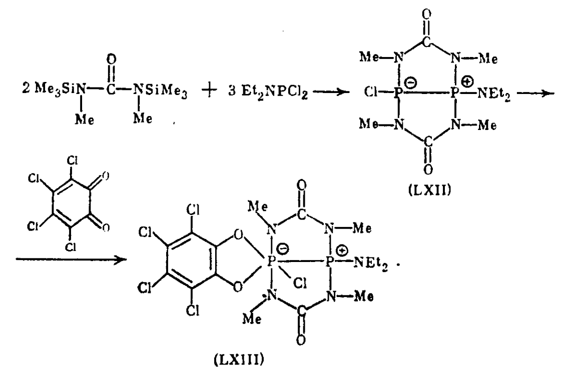
The authors[86] suggest that the equilibrium (LX) ⇌ (LIX) occurs in the system, as shown by the observation of two signals in the ^{31}P NMR spectra—at -14.5 p.p.m. for (LX) and at -96.2 p.p.m. for (LIX) in proportions of 2 : 3.

The interaction of *N*-t-butyldiethanolamine with the amide or chloride of phenylenephosphorous acid leads only to a phosphorate of type (LXI).[87] An equilibrium mixture of the phosphorate (LXI) with the P–OH fragment and the phosphate has been obtained in the reaction of phosphorous acid containing the 1,3,6,2-dioxazaphosphocane ring with tetrachloro-*o*-benzoquinone:[86]



(LXI)

In order to synthesise tricyclic phosphorates, dicarbonyl compounds have been made to interact not only with cyclic phosphites but also with cyclic phosphonium compounds. Thus the first phosphorate (LXIII) with a P–P bond has been obtained by adding chloranil to the anionoid phosphorus atom in the condensed bicyclic structure (LXII):

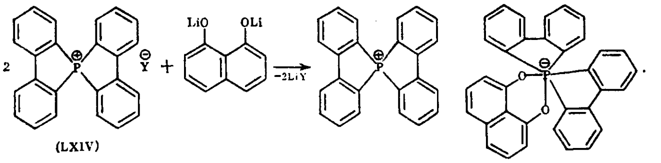


(LXII)

(LXIII)

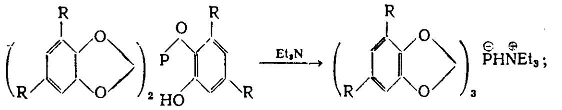
The chlorine atom at the phosphorus atom can be exchanged for fluorine by treatment with arsenic trifluoride (but not sodium fluoride).[88]

The spirocyclic phosphonium salt (LXIV) interacts with salts of catechol or naphthalene-1,8-diol, forming a phosphorate in which the P(VI) atom is part of two phospholan rings and one 1,3,2-dioxaphosphorinane ring:[75]



(LXIV)

The phosphorane (LXV) has been obtained by the reaction of 3,5-di(t-butyl)-o-quinone with white phosphorus in the presence of 3,5-di(butyl)catechol as the reductant.[89] The addition of triethylamine to compound (LXV) induces the precipitation of the phosphorate (LXVI), which is also formed in the reaction of phospha(III)adamantane with the same o-quinone:[90]



(LXV) (LXVI)

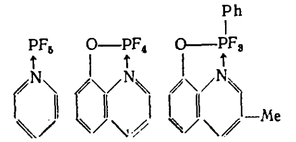
R=C(Me)$_3$.

The thermolysis of the dimer $(MeNPF_3)_2$, which results in the formation of complex polyhedral structures incorporating hexacoordinate phosphorus atoms, has been described.[91]

III. MOLECULAR STRUCTURE AND DYNAMIC STEREOCHEMISTRY

X-Ray diffraction analysis of acyclic,[92–94] monocyclic,[15,18,19,26–28,30,35] spirobicyclic,[45] and spirotricyclic[44,70] hexacoordinate phosphorus compounds made it possible to establish unambiguously their tetragonal-bipyramidal structure with a greater or smaller distortion of the octahedral skeleton, depending on the nature of the ligand bound to the central P(VI) atom.

The length of the N–P bond in the nitrogen-containing P(VI) complexes, formed via the intermolecular [as in compound (LXVII)] or intramolecular [as in compounds (LXVIII) and (IV)] binding of the nitrogen atom to phosphorus, is greater than the length of the usual single nitrogen–phosphorus bond (1.769 Å).[18,19,94]



(LXVII) (LXVIII) (IV)

An appreciable weakening of the N → P bond has been observed in the series of neutral P(VI) complexes (IV), (LXVII), and (LXVIII): 1.898 Å for (LXVII), 1.911 Å for (LXVIII), and 1.980 Å for (IV), owing to the decrease of the Lewis acidities of the groups in the sequence $PF_5 > POF_4 > POF_3Ph$. It is striking that the influence of other ligands is also reflected in the length of the P–F bond. Thus the length of the P–F bond in compound (LXVIII) diminishes with decrease of the electronegativity of the *trans*-ligand in the sequence F–P(F) > F–P(←N) > F–P(O).[18]

A significant distortion of the regular octahedral geometry, expressed by the deviation of the PF^1, PF^2, and PO bonds from the P–C bond, has been observed in the molecular structure (IV). This may be a consequence of the repulsion of the coplanar P–O and P–F bonds from the P–C bond, which is characterised by a high electron density in the latter.[19] A similar deviation of the fluorine atoms from the nitrogen atom has been observed in the complex (LXVII).[94]

An increase in the length of the phosphorus–nitrogen bonds (1.91 and 1.85 Å) compared with the single bond has been found also in the four-membered ring of the zwitterionic complex (XIX).[30] On the other hand, the C–N bonds are much shorter (1.34 and 1.19 Å) than the usual bond (1.48 Å) and this suggests the delocalisation of the positive charge in the N–C–N triad and the partial double bond character of the C–N bonds. One of the causes of the formation of the "long" P–N bonds in compound (XIX) may be the angular strain in the four-membered phosphorus-containing heterocycle.

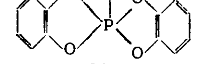
For the same reason, the P–O bonds in the complexes (XVI) are appreciably longer (1.82 and 1.89 Å) compared with the phosphorate (XLIa).[26,27] The electron density in these compounds is also delocalised in the carbamate unit, which is indicated by the smaller lengths of the C–O bonds (1.29 and 1.30 Å) compared with the usual bond (1.43 Å) and by the significant shortening of the C–N bond involving the bridgehead carbon atom (1.33 Å); the terminal C–N bonds are considerably longer (1.48 and 1.49 Å). The small difference between the lengths of the P–O bonds is associated with the *trans*-influence of the Me and CF_3 groups. The P–O bond in the *trans*-position with respect to the relatively small electron-accepting trifluoromethyl substituent is somewhat shorter than the O–P(Me) bond.

The fluorophosphorates $F_{4-n}(CF_3)_nPO_2CNMe_2$ have an analogous steric structure. The trifluorophosphorate ($n = 1$) has been isolated in the form of two structural isomers with "equatorial" and "axial" CF_3 groups. One isomer has been observed for each of the compounds with $n = 2$ and $n = 3$, X-ray diffraction of the monofluoroderivatives demonstrating the "equatorial" disposition of the fluorine atom; the carbamate ring, the fluorine and phosphorus atoms, and the carbon atom of one of the CF_3 groups are coplanar. The length of the P–O(F-*cis*) bond (1.832 Å) exceeds somewhat the length of the other bond, namely P–O(F-*trans*) (1.788 Å).[28]

The difference between the lengths of the P–O bonds (1.706 and 1.723 Å) in the five-membered phenylenedioxy-rings of the *tris*(*o*-phenylenedioxy)phosphorate anion (XLIa) reflects some distortion of the octahedral structure of the phosphorate. The endocyclic OPO angles (91.4°) are close to the right angle, indicating the absence of angular strain.[70]

At the same time the increase of the length of the endocyclic ether bonds compared with the exocyclic bonds is evidently in general characteristic of small rings incorporating a phosphorus atom and heteroatoms with an unshared electron pair.[45] Thus the exocyclic P–O bonds in the phosphorate (XXV) are appreciably shorter (1.656 Å) than the endocyclic bonds (1.711 Å). According to the authors,[45] this may indicate a greater degree of $(p-d)_\pi$ binding of the unshared electron pairs of the exocyclic oxygen atoms to the phosphorus atom compared with the endocyclic atoms. This effect, which has also been established in phosphorane molecules, is called "steric inhibition of $(p-d)_\pi$ bonding".[45] It has been suggested[45] that this may entail a decrease of the shielding of the phosphorus nuclei by the electrons, which is reflected in a shift of the ^{31}P signal in the NMR spectra towards weaker magnetic fields, observed when one or several five-membered rings are introduced into hydroxyphosphorane molecules:

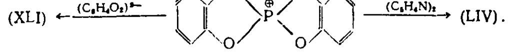
$(PhO)_5P$



$\delta(^{31}P) = -88.7$ p.p.m. -30 p.p.m.

In phosphorate molecules a tendency has also been observed towards decreased shielding of phosphorus on passing from acyclic [$\delta(^{31}P) = -142$ p.p.m. for $(MeO)_6P^-K^+$ [9] and -147 p.p.m. for $(EtO)_6P^-K^+$ [9]] to monocyclic [-128 p.p.m. for (XXI) [33]], bicyclic [-109.5 p.p.m. for (XXV) [41] and -98 p.p.m. for (XXXI, R^2 = OPh) [50]], and tricyclic [-82 p.p.m. for (XLI, A = Na) [75] and -89 p.p.m. for (XLVII) [70]] phosphorates.

A distorted octahedral configuration has also been found in the cationic bipyridyl P(VI) complex (LIV).[44] The unusual features of its structure can be clearly revealed by comparing it with the structure of the phosphorate (XLI) and the hypothetical spirocyclic phosphonium cation (LXIX), from which compounds (XLI) and (LIV) can be produced formally by the addition of the bidentate phenylenedioxy- and bipyridyl ligands respectively:[44]

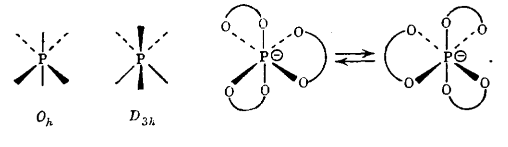


(LXIX)

The P–O bonds in the cation (LIV) are shorter by 0.045 Å and the endocyclic OPO angles are greater by 1.6° than in compound (XLI). The OPO axis, which is almost straight in compound (XLI), bends in compound (LIV) towards the bipyridyl ligand (172.7°). The imaginary addition of the phenylenedioxy-dianion to the tetrahedral phosphorus in the cation (LXIX) yields a P(VI) configuration which is close to the octahedral P(VI) configuration in compound (XLI). An analogous change in the geometry of the molecular skeleton should also occur in the transition (LXIX) → (LIV), but, since the bipyridyl ligand is a weaker electron donor than the catechol dianion, the features of the "tetrahedral" configuration are retained in the structure (LIV).[44]

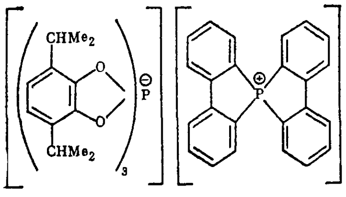
X-Ray diffraction data for the only cyclic six-membered λ^6-1,3,2-diheterophosphorinane investigated by this method, namely the acetylacetonate complex (II), indicate only small changes in the length of the P–O bond compared with those in compound (XLI), i.e. the P–O bonds in the dioxaphosphor(VI)inane ring are also of the σ-type. The ring has the boat conformation with the phosphorus and C(5) atoms deviating from the plane of the remaining atoms.[19]

Thus an octahedral O_h geometry is characteristic of phosphorate structures, as for many other molecules incorporating elements with a coordination number of six.[95] Recent calculations for the hypothetical PH_6^- molecule have shown[96] that this geometry is more stable than the alternative prismatic geometry with the D_{3h} symmetry:

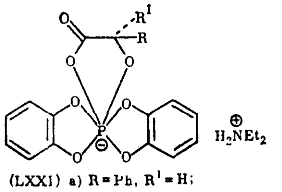


(1)

The tris-chelate hexacoordinate structures, including phosphorate anions, are chiral and exhibit the enantiomeric equilibrium (1) in solutions. The diastereotopic nature of the methyl groups in the isopropyl groups of compound (LXX) (two doublets with δ = 0.86 and 1.03 p.p.m., $^3J_{hh}$ = 7 Hz) confirms this postulate.[97] The study of the ^1H and ^{31}P spectra of the phosphorates (LXXI) led to an analogous conclusion:[98]



(LXX)



(LXXI) a) R = Ph, R^1 = H;
b) R = R^1 = Me.

The phosphorus atom in compound (LXXIa) gives rise to two signals in the region of -90 p.p.m. and the difference between the chemical shifts is 0.5 p.p.m. The proton of the aliphatic ligand resonates in the form of two doublets with $\delta(A)$ = 5.33 p.p.m. and $\delta(B)$ = 5.19 p.p.m. At the instant of the synthesis of compound (LXXIa) at room temperature, the isomer ratio (B) : (A) = 25 : 75, varying with time to 44 : 56. Coalescence of the doublet is observed at 120 °C.

The study of the kinetics of the epimerisation of the optically active P(VI) compounds by the polarimetric and NMR method made it possible to determine the free energies of activation for the unimolecular epimerisation process $\Delta G^\# = 20.5$ kcal mol^{-1} for (LXXIa) and 21.7 kcal mol^{-1} for (LXXIb), whose rate increases with increase of the concentration of the test substances.[98,99] The epimerisation of phosphorates is characterised by low activation entropies and, as noted for phosphorates of type (LXXI), is accelerated in the presence of acids.[100]

Two mechanisms of the enantiomeric isomerisation (and in general of polytopic processes) of octahedral structures has been discussed: the regular mechanism unaccompanied by the dissociation of the bond between the central atom and the ligand and the irregular mechanism which takes place with cleavage of the element–ligand bond. In the former case the ligand isomerisation process proceeds in accordance with the trigonal twist mechanism via a transition state having the pyramidal D_{3h} structure,[96,101] while in the second case the process proceeds via intermediates with a pentcoordinate central atom.

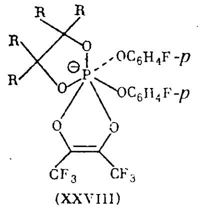
Calculation of the barriers to the topomerisation of simple molecules[95,96] demonstrated that the regular mechanism is energetically unfavourable. Thus the energy barriers to the trigonal twist E amount to -66 kcal mol^{-1} for PF_6^-, -56 kcal mol^{-1} for PCl_6^-, and -41 kcal mol^{-1} for PH_6^-, which indicates the stereochemical rigidity of the octahedral O_h structures for atoms of non-transition elements. It is difficult to say to what extent these calculated data are applicable to complex real systems containing oxygen and nitrogen atoms as well as chelated ligands, but one should note that the replacement of hydrogen atoms by more electronegative atoms or groups increases the activation barrier.[101]

The experimental results of the study of the kinetics of the epimerisation of phosphorates presented above led the authors[98–100] to the conclusion that the isomerisation has the irregular mechanism. The process proceeds with dissociation of one of the ether bonds in the aliphatic five-membered ring, pseudorotation in the phosphorane intermediate, and subsequent recyclisation leading to the formation of the second enantiomer. The free energies of epimerisation found fall within the range characteristic of ligand reorganisation processes involving phosphoranes (14–22 kcal mol^{-1}).[96,102] The low activation entropies agree with this conclusion and the concentration effects found are associated with the variation of the ionic strength of the solution, which influences the dissociation of the bonds and the charge separation.[98]

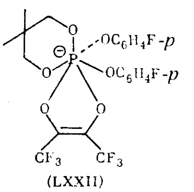
An analogous epimerisation mechanism has been proposed for neutral P(VI) chelates (LVI): the $\Delta G^{\#}$ for these processes fall within the range indicated above: 18.1 kcal mol^{-1} for (LVI, R = C_5H_4N) and 17.3 kcal mol^{-1} for (LVI, R = Ph).[47]

At the same time the irregular permutation process has been postulated for the *cis–trans* isomerisation of the phosphorates (XXVIII), investigated by ^{19}F NMR.[47] At room temperature these compounds are characterised by the energetically favourable *cis*-disposition of the aryloxy-ligands. However, at -101 °C the CF_3 groups in the phosphorate (XXVIIIb, R = Me) give rise to signals at -0.49 and -0.75 p.p.m., while p-FC_6H_4O generates signals at -60.2 and -61.7 p.p.m. The CF_3 signals coalesce reversibly at -77 °C ($\Delta G^{\#}$ = 9.7 kcal mol^{-1}), whereas for p-FC_6H_4O coalescence is observed at 34 °C ($\Delta G^{\#}$ = 14.5 kcal mol^{-1}). For the analogous *cis*-anion (XXVIIa, R = H), the free energy of activation determined from the coalescence of the signals of the trifluoromethyl group, is 17.2 kcal mol^{-1} (T_c = 80 °C). In the case of the 1,3,2-dioxaphosphor(VI)inane anion (LXXII), the signals of the CF_3 groups coalesce at 3 °C ($\Delta G^{\#}$ = 13.1 kcal mol^{-1}), whereas the signals of the p-FC_6H_4O groups remain separated up to 60 °C ($\Delta G^{\#}$ > 16 kcal mol^{-1}).

Thus the energy barriers to "equilibration" in the phosphorates (XXVIIIa, b) and (LXXII) are different for different magnetically non-equivalent groups—CF_3 and p-FC_6H_4O. This can be explained from the standpoint of the formation of different trigonally-prismatic intermediates in the above processes:

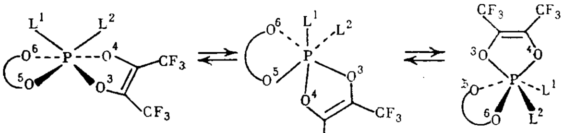


(XXVIII)
R = H (a); Me (b)



(LXXII)

Scheme 1

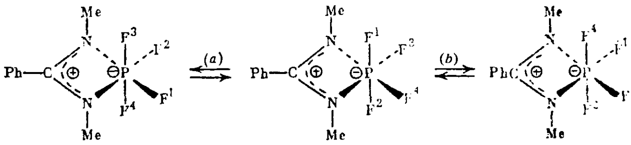


(LXXIV) (LXXIII) (LXXV)

In the structure (LXXIII, L = p-FC_6H_4O) the 60° clockwise rotation of the (2,4,3) trio relative to the (1,5,6) trio leads to the trigonal prism (LXXIV) in which the CF_3 groups are equivalent and there is no p-FC_6H_4O (Scheme 1). On the other hand, the 60° anticlockwise rotation of the (1,2,3) trio relative to the (4,5,6) trio generates the trigonal prism (LXXV) with the equivalent fluorophenoxy-groups and non-equivalent trifluoromethyl groups. Other possibilities involving a trigonal twist (there are eight in all—not shown in the Scheme) have an analogous effect on both types of F atoms. The observed experimental results are believed[47] to agree well with the regular permutation polymerisation process. The retention of the values of J_{PF} for structures (XXVIII) and (LXXII) confirms the intramolecular character of this topomerisation.

The permutation isomerisation of *NN*-dimethylbenzamidinium tetrafluorophosphorate (LXXVI), as a result of which the mutually non-equivalent F(1,2) and F(3,4) atoms change places in the tetragonal bipyramid according to ^{19}F NMR data, is also intramolecular.[103] This is indicated by the retention of the $^{31}P-^{19}F$ and $^{31}P-^{1}H$ spin–spin coupling and also by the absence of an influence of the concentration of the test substance in solution and by the nature of the solvent on the rate of isomerisation

Scheme 2



(LXXVIa) (LXXVI) (LXXVIb)

Two alternative isomerisation mechanisms were discussed in this instance also: irregular and regular. The irregular mechanism can in its turn include the dissociation of the phosphorus–nitrogen bond, which leads to structure (LXXVIa) (Scheme 2), in which all four fluorine atoms change places (pathway *a*) or the dissociation of the P–F bond with migration of, for example, the F^2 atom to the cationoid carbon. In this case (pathway *b*) the positions of three F atoms change and structure (LXXVIb) is formed (the intermediate structures are not shown in Scheme 2). For the regular mechanism, it is also possible to put forward several versions of the trigonal twist, but the exchange of all fluorine atoms is preferred to the greatest extent [pathway *a* leading to (LXXVIa)].

The fairly high free energy of activation for the permutation isomerisation of compound (LXXVI) (23.6 kcal mol^{-1} at 170 °C) exceeds the values characteristic of the polytopic rearrangements of phosphorates. In view of this and also the independence of the rate of isomerisation of the nature of the solvent the authors are inclined[103] to select the regular mechanism via pathway *a* (LXXVI) → (LXXVIa), although the available data are as yet insufficient for an unambiguous conclusion.

Thus one may decide that, on the basis of what are so far still few instances of the study of polytopic rearrangements of P(VI) compounds, it is impossible to arrive at reliable conclusions about their mechanism. However, one cannot rule out the possibility that the character of the ligand reorganisation in phospha(VI)cyclanes can depend greatly on their structure—the nature of the atoms attached to phosphorus and the number, size, and compositions of the phosphorus-containing heterocycles. One can only note that the irregular mechanism is believed to be preferred for spirotricyclic phosphorates, while the regular mechanism is preferred for spirobicyclic and monocyclic phosphorates.

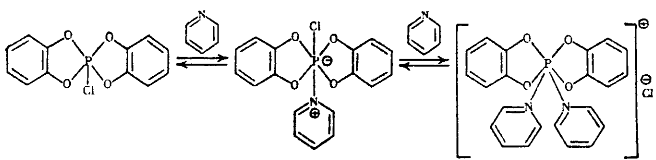
IV. P(VI) ⇌ P(V) EQUILIBRIUM PROCESSES

The capacity for the rupture of one of the P(VI)–ligand bonds, which is responsible for the possibility of the intramolecular or intermolecular P(V) ⇌ P(VI) equilibrium processes, is characteristic of certain hexacoordinate phosphorus compounds.

When the tautomeric mixture (XXXVIa, b) interacts with pyridine, a successive decrease of the intensity of the low-field NMR signal of the P(III) atom in the form (XXXVIa) and an increase of the peak intensity in strong fields, reflecting the content of the P(V) form (XXXVIb) and the P(VI) form (XXXVII), are observed as the mole fraction of the base increases and the temperature is reduced. An appreciable excess of the base at room temperature shifts the resonance peak to the "phosphorate" region (-93 p.p.m. for 8 moles of pyridine).[42,61,62]

The position of the P(III) ⇌ P(V) ⇌ P(VI) equilibrium is significantly affected also by the basicity of the amine. The weak base diphenylamine does not induce appreciable changes in the ^{31}P NMR spectrum, while in the presence of tertiary and secondary aliphatic amines the signals due to the P(III) and P(V) forms disappear and high-field doublets appear at −110 p.p.m. (J_{PH} = 800 Hz).[63]

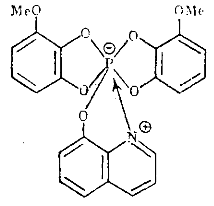
The addition of pyridine to the chlorophosphorane (LXXVII) is also accompanied by a shift of the (LXXVII) signal (−9.5 p.p.m.) to a strong field (−84.5 p.p.m.):



(LXXVII) (LXXVIII) (LXXIX)

It has been suggested[43] that the reversible addition of the base molecule [(LXXVII) ⇌ (LXXVIII)] takes place without a significant reorganisation of the (LXXVII) molecular skeleton and requires only a low activation barrier to be overcome. This is responsible for the lability of the above equilibrium and for this reason the average signal of both forms, (LXXVII) and (LXXVIII), is observed. However, after the addition of even the first portions of pyridine, the (LXXIX) signal is observed at −100 p.p.m., together with the −84.5 p.p.m. peak, its intensity increasing with increase of the mole fraction of pyridine on reaching a maximum in the presence of a twofold excess of the base. The (LXXVIII) → (LXXIX) transition represents a substitution reaction and requires a higher activation barrier to be overcome. In the presence of an excess of pyridine the cationic P(VI) compound (LXXIX) crystallises quantitatively.

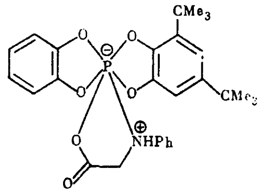
The capacity of phosphoranes to be converted into phosphorate structures is manifested most distinctly in the formation of the intramolecular P–N bond. Compound (LXXX) exist in the P(VI) form even at room temperature [δ(^{31}P) = 78 p.p.m.].[62]



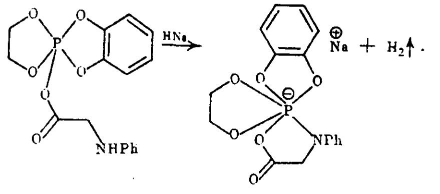
(LXXX)

The study of factors determining the capacity for intramolecular N → P complex formation in systems of type (LXXX) has demonstrated a strong influence of the nature of the ligands on the tendency towards the formation of phosphorates. The electron-accepting properties of the substituents at the phosphorus atom play a decisive role in this connection. Thus, when one fluorine atom is replaced by an alkyl group in the molecule of compound (IV), the N–P bond is not formed and the difluoro-derivative exists exclusively in the form of the difluorophosphorane, while tri- and tetrafluoro-analogues exist only in the P(VI) form.[18]

Two arylenedioxy-substituents have a strong positive influence on the phosphorus atom, so that compound (LXXXI) is characterised by a high-field signal [δ(^{31}P) = 89 p.p.m.]. The introduction of the aliphatic ethylenedioxy-group instead of the phenylenedioxy-ligand results in the existence of only the P(V) form—the phosphorus atom in the structure (LXXXII) is pentacoordinated. However, when compound (LXXXII) is acted upon by sodium hydride, it is converted into the phosphorate (LXXXIII).

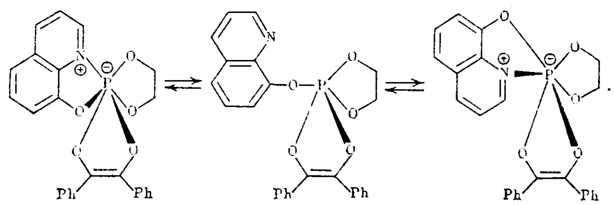


(LXXXI)



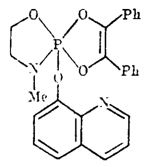
(LXXXII) δ(^{31}P) = −28 p.p.m. (LXXXIII) δ(^{31}P) = −83 p.p.m.

The high-field signal can reflect the P(V) ⇌ P(VI) equilibrium, which is as a rule established rapidly on the NMR time scale and for this reason both forms are manifested by a single average signal, whose increasingly upfield shift implies an increase in the content of the P(VI) compound in the equilibrium mixture. Thus the resonance peak for compound (LXXXIV) in the region of −85 p.p.m., recorded at 20 °C, is observed in weak fields (−75 p.p.m.) at 150 °C and, conversely, on reducing the temperature to −70 °C, the signal undergoes an upfield shift to −88.7 p.p.m., while at −90 °C an additional resonance line appears at −90.6 p.p.m. It has been suggested[85] that a decrease of temperature shifts the equilibrium towards the P(VI) isomer, which exists in the two diastereoisomeric forms (LXXXIVa) and (LXXXIVb), with corresponding doubling of the signal at −90 °C.

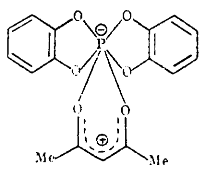


(LXXXIVa) (LXXXIV) (LXXXIVb)

It is striking that replacement of the endocyclic oxygen atom in the ethylenedioxy-fragment of compound (LXXXIV) by the more electron-donating NMe group lowers the Lewis acidity of the phosphorus atom and the oxazaphospha(VI)-cyclane (LXXXV) is a phosphorane [δ(^{31}P) = −43.7 p.p.m.]



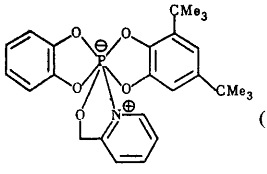
(LXXXV)

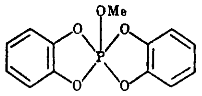


(LXXXVI)

Comparison of the structures of compounds (LXXXII) and (LXXXIV) also indicates the importance of the effects of electron delocalisation in the stabilisation of hexacoordinate structures. The π-electron system of the hydroxyquinoline ligand, which promotes the delocalisation of electron density, favours the P(VI) form more than does the aliphatic structure of *N*-phenylglycine. The relative instability of the P(VI) acetylacetonate compound (LXXXVI) is explained by the fact that the delocalisation of electron density is restricted to the region within the non-polar 1,3,2-dioxaphospholan ring.[85]

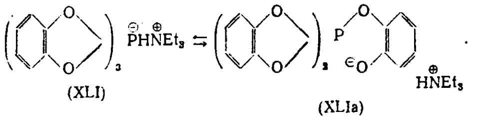
The influence of the entropy factor on the position of the P(V) $\rightleftharpoons$ P(VI) equilibrium, which is more significant for intermolecular complex formation ($\Delta S_0 = -30$ e.u.) than for intramolecular complex formation (−10 e.u.), has been noted.[85] In particular, as a result of this complex formation is not observed in the pyridine–phosphorane (LXXXVIII) system if compound (LXXXVII) exists mainly in the P(VI) form.


(LXXXVII) $\delta(^{31}P) = -86$ p.p.m.


(LXXXVIII) $\delta(^{31}P) = -26$ p.p.m. (pyridine)

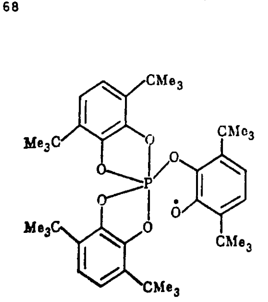
Finally, mention must be made of the role of steric effects of the substituents in the ligand. Thus the introduction of a methyl substituent in the 2-position in the hydroxyquinoline fragment in compound (LXXX) shifts the equilibrium towards the P(V) form, which has been explained by the repulsion of the methyl group and one of the oxygen atoms of the benzodioxaphospholan rings. This hinders the closure of the oxazaphospholan ring (the formation of an N → P bond).[85]

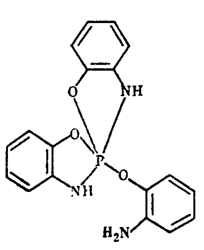
It has been suggested that the P(V) $\rightleftharpoons$ P(VI) equilibrium obtains also in the tri(phenylenedioxy)phosphorate anion (XLI) and is displaced towards the phosphorane (XLIa) in solution and towards the phosphorate in the crystalline phase:[66]


(XLI) (XLIa)

A sextuply degenerate rearrangement with "random wandering" of the charge over the aromatic ligands obtains in this instance.[95,104] However, the rate of such "random wandering" is low on the NMR time scale, so that the single average chemical shift due to the P(V) and P(VI) nuclei as well as the protons of the aromatic ring is observed in the spectra.

Such intramolecular degenerate tautomerism, associated with the "random wandering" of the free valence over the aromatic fragments, has been observed for the stable radicals having the octahedral P(VI) structures (LXXXIX).[104] On the other hand, the nitrogen compound (XC), having a analogous structure, exists in the phosphorane form, although the authors do not reject the possibility of formation of the corresponding phosphorates in the crystalline state.[68]

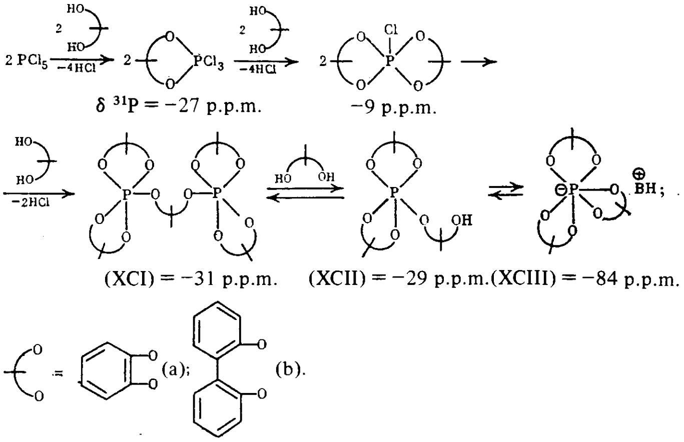

(LXXXIX)


(XC) $\delta(^{31}P) = -46.3$ p.p.m.

It has been established in many instances that the conjugate acid (XCIIa) of the anion (XCIa) and its analogues are intermediates in the synthesis of phosphorates from the corresponding phosphoranes and diols, usually catechol (see Section II). The transition (XCII) → phosphorate (XCIII) is a prototropic process associated with the intermolecular proton transfer to an "external" base, as in ring closure in hydroxyalkyl (aryl) phosphates.[12]

The study of the interaction of PCl_5 with catechol and 2,2′-dihydroxybiphenyl established the occurrence of the stepwise substitution of the chlorine atoms including the prototropic equilibrium P(V) $\rightleftharpoons$ P(VI)[74] (Scheme 3)

Scheme 3

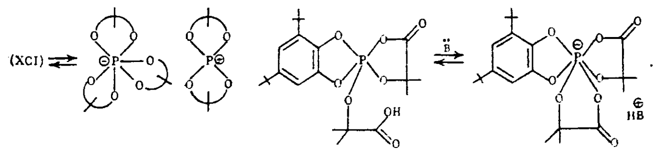

δ ^{31}P = −27 p.p.m. −9 p.p.m.

(XCI) = −31 p.p.m. (XCII) = −29 p.p.m.(XCIII) = −84 p.p.m.

(a); (b).

When the PCl_5 : catechol ratio is 1 : 2.5, the deposition of a crystalline deposit of compound (XCI) is observed. The latter is redissolved by an excess of catechol. The existence of the equilibrium (XCI) $\rightleftharpoons$ (XCII) (the ratio of the compounds involved was 8 : 2 in benzene) has been established by NMR. The addition of DMF to this mixture induces a gradual shift of the signal of compound (XCII) (−29 p.p.m.) to the region of −84 p.p.m. of compound (XCIII) and a decrease of intensity followed by the disappearance of the −31 p.p.m. signal of the compound (XCI). This corresponds to the process (XCI) $\rightleftharpoons$ (XCII) $\rightleftharpoons$ (XCIII), in which the equilibrium between the last two compounds is attained rapidly on the NMR time scale.

Koenig et al.[74] also did not rule out the existence in solutions of an equilibrium between compound (XCI) and the ion pair (XCIa), which has been confirmed by the ebullioscopic determination of the molecular weight of this compound:

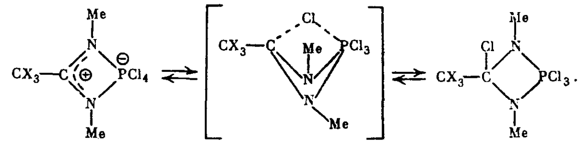

(XCIa) (XCIV) (XCV)

The conversion of the ω-hydroxyalkylphosphorane into a phosphorate has been observed in systems constructed with the aid of hydroxyacid ligands. In toluene the equilibrium (XCIV) $\rightleftharpoons$ (XCV) is fully displaced towards the phosphorane (XCIV), while in DMF and DMSO it is displaced towards the spirophosphorate (XCV).[105]

The action of strong bases on the (XCI) $\rightleftharpoons$ (XCII) equilibrium mixture leads to the formation of the insoluble phosphorates (XCIII). The use of the chiral base (−)-brucine in this reaction[74] made it possible to observe the signals of two diastereoisomeric brucinium phosphorates (−84.4 and

and −84.5 p.p.m.), which are in equilibrium. A kinetic study of the epimerisation of these diastereoisomers led the authors[74] to the conclusion that the P(VI) anion is obtained in the synthesis in a non-racemic form and that the P(V) → (VI) transformation is therefore stereospecific. The results obtained[74] agree well with the concept of the occurrence of degenerate tautomeric processes with participation of spirobicyclic and tricyclic anions of type (XLI).

The first example of chlorotropic tautomerism with participation of pentacoordinate and hexacoordinate phosphorus compounds has been described recently:[22]

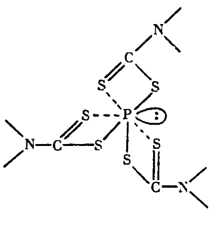


(XCVI) X = Cl (a); F (b) (XCVII)

The equilibrium (XCVIa) ⇌ (XCVIIa) is attained fairly slowly on the NMR time scale: the signals of both forms can be detected in the spectra. As the CX_3 group becomes more electron accepting (CF_3 > CCl_3), the solvent polarity decreases, the temperature rises, and the equilibrium is displaced towards phosphoranes. Thus at 30 °C the content of the P(V) form (XCVIIa) is 60% in CD_3CN, 84% in $C_6H_4Cl_2$-o, 87% in C_6H_6, and 97% in C_6D_{12}; at 50 °C the content of the P(V) tautomer in CD_3CN increases to 66%. The signals of the methyl protons coalesce at 120 °C. The independence of the rate of interconversion of the tautomeric forms of concentration indicates the intramolecular character of the tautomerism and suggests a structure with a bridging chlorine atom and a hexacoordinate phosphorus atom as the transition state or the intermediate.

The equilibrium processes with participation of pentacoordinate and hexacoordinate forms of organophosphorus molecules examined here model satisfactorily the first stage of the associative nucleophilic substitution of the pentacoordinate phosphorus, which presupposes the addition of the nucleophile to the P(V) atom of the substrate with formation of hexacoordinate intermediates and/or transition states.[12]

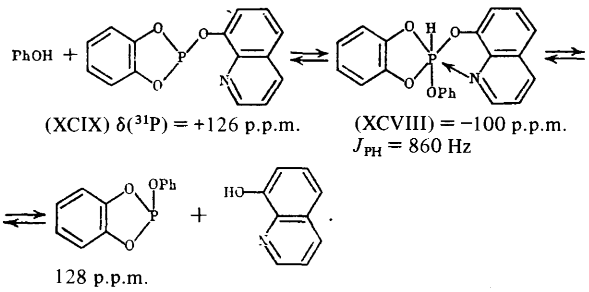
The question of the character of the intermediates or transition states in nucleophilic substitution reactions at a hexacoordinate phosphorus atom is therefore intriguing. The substitution of chlorine in compound (LXXVII) by a pyridine molecule with formation of the dipyridine P(VI) cation (LXXIX)[43] is one of the few examples of such reactions. The process is most likely to proceed via a dissociative mechanism with the preliminary elimination of the chloride anion. The associative mechanism appears unlikely: not a single example of the existence of structures with a phosphorus atom surrounded by seven ligands has so far been discovered. In the tris(dithiocarbamato)phosphines,[106,107] trisdithioacylates, and phosphinodithioyl derivatives of other group VB elements[108–110] described hitherto, a coordination number of seven of the central atom is attained by the formation of three sulphur–element coordinate bonds by virtue of the presence of a stereochemically active unshared electron pair of the element.



V. CYCLIC COMPOUNDS OF HEXACOORDINATE PHOSPHORUS AS INTERMEDIATES IN THE REACTIONS OF ORGANOPHOSPHORUS COMPOUNDS

It has been suggested and in many cases demonstrated that λ^6-1,3,2-diheterophosphacyclanes can be intermediate in reactions of organophosphorus compounds containing the atoms of tricoordinate, tetracoordinate, or pentacoordinate phosphorus. The involvement of P(VI) intermediates in the reactions of tervalent phosphorus compounds has been demonstrated only in some instances and is more likely to be an exception rather than the rule.[10] The intermediate formation of hexacoordinate phosphorus compounds occurs only in specific cases—in reactions of bifunctional or polyfunctional reactants or substrates.

The formation of the intramolecular P(VI) complex (XCVIII) in the transesterification of the phosphite (XCIX) with phenol has been detected from ^{31}P NMR spectra: the signal of compound (XCVIII) with $\delta(^{31}P) = -100$ p.p.m. and $J_{PH} = 860$ Hz, whose intensity is high at the beginning of the reaction and decreases as the latter is completed, has been detected at −70 °C in methylene chloride:[111]

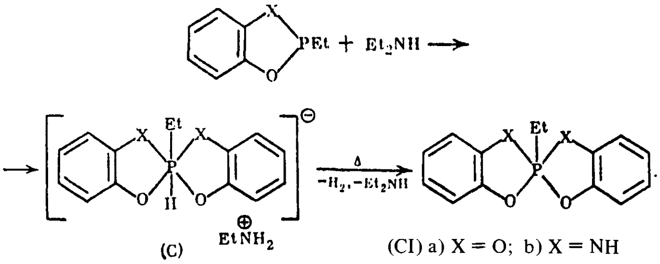


(XCIX) $\delta(^{31}P) = +126$ p.p.m. (XCVIII) = −100 p.p.m. $J_{PH} = 860$ Hz

128 p.p.m.

The stabilisation of compound (XCVIII) is achieved as a result of the presence of the 1,3,2-benzodioxaphospholan ring and the possibility of the formation of intramolecular P → N bonds.

The spirobicyclic phosphorate (Ca) has been isolated in 15% yield in the reaction of 2-ethyl-4,5-benzo-1,3,2-dioxaphospholane with diethylamine.[60] On heating, the salt (Ca) evolves a hydrogen molecule and is converted into the phosphorane (CIa). The same result has been obtained in the reaction of catechol with ethylphosphonous bis(diethylamide):



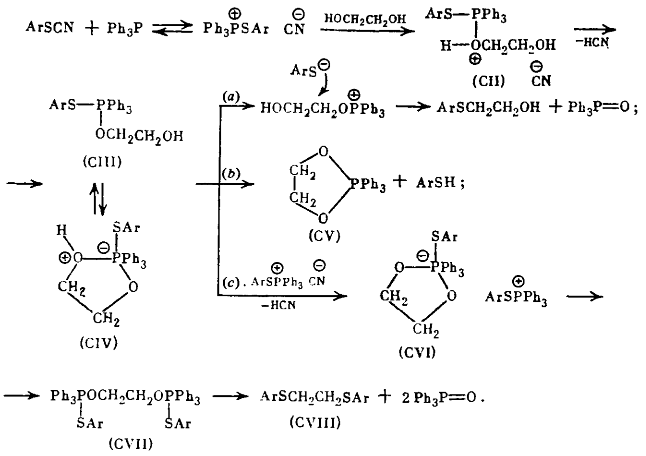
(C) (CI) a) X = O; b) X = NH

The interaction of o-aminophenol, leading to the phosphorane (CIb), can take place via the same pathway. However, the corresponding aminophosphorate could not be isolated owing to its smaller stability [see structure (XC)].

The results of the reactions of aryl thiocyanates with alcohols and diols in the presence of triphenylphosphine has been explained by the involvement of pentacoordinate and hexacoordinate phosphorus intermediates. The interaction of phenyl thiocyanate with triphenylphosphine and ethylene glycol takes place via pathway a (Scheme 4) and leads to 2-phenylthioethanol and triphenylphosphine oxide.[112]

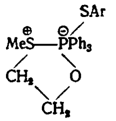
Aliphatic alcohols react analogously with formation of alkyl aryl sulphides.[113] On the other hand, another pathway (pathway *b*), leading to the isolation of *p*-methoxybenzenethiol and the cyclic phosphorane (CV), is also followed in the reaction with participation of *p*-methoxyphenyl thiocyanate. It has been suggested[112] that the oxonium–phosphorane adduct (CII) is a key intermediate in these processes.

Scheme 4



Its deprotonation by the cyanide ion affords the phosphorane (CIII); the decomposition of compounds of type (CIII) via pathway *a* is responsible for the formation of sulphides in the reactions of alcohols and of 2-phenylthioethanol in the reaction of ethylene glycol. The *p*-methoxyphenylthio-group is difficult to eliminate compared with the phenylthio-substituent and for this reason the attack by the terminal hydroxy-group on the pentacoordinate phosphorus atom competes with elimination of the arylthio-group from the phosphorane (CIII, Ar = p-MeOC$_6$H$_4$) (pathway *a*). This leads to the cyclic dipolar phosphorate (CIV); the fragmentation of the latter leads to the *p*-methoxybenzenethiol and the cyclic phosphorane (CV) (pathway *b*).

The possibility of the formation of the phosphorate (CIV) in these processes has been confirmed by the synthesis of aryl methyl sulphide in the reaction of *p*-methoxyphenyl thiocyanate with 2-methylthioethanol ($MeSCH_2CH_2OH$), which proceeds via the intermediate (CIX), which is analogous to the intermediate (CIV):



(CIX)

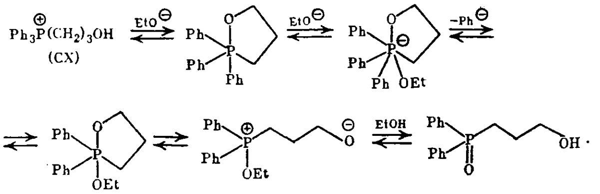
The involvement of *p*-nitrophenyl thiocyanate in this reaction does not lead to the formation of the sulphide, because the nucleophilicity of the arylthio-group is in this case insufficient for the demethylation of compound (CIX, Ar = p-NO$_2$C$_6$H$_4$) and the process proceeds in the "normal" way via pathway *a* to the bis-sulphide $MeSCH_2CH_2SC_6H_4NO_2$-*p*.

An essential condition for the formation of the phosphorate intermediate (CIV) from compound (CIII) is the presence of a free hydroxy-group, since glycol monoethers react only via pathway *a*, like primary alcohols.[112]

The *p*-nitro-substituent in the aryl group stabilises the negative charge on the phosphorus atom in the phosphorate (CIV) and the possibility of yet another competing pathway (pathway *c*) arises in this case; it is associated with the deprotonation of the phosphorate (CIV) by cyanide ion and the appearance of the ion pair (CVI). The interaction of the ions of the pair (CVI) leads to the bis-sulphide (CVIII) via the bisphosphorane (CVII) stage.

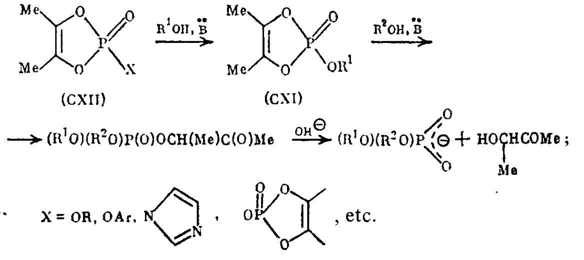
When the nitro-group is introduced in the *o*-position in the benzene ring, the formation of compound (CIV) is hindered for steric reasons and the process is therefore wholly directed via pathway *a*. The same results have been observed when 1,3- and 1,4-diols were used. Evidently the formation of phosphorates with a greater ring size than in compound (CIV) is energetically unfavourable.

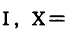
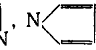
An analogous intermediate formation of a five-membered ring in the P(V) and P(VI) intermediates ensures a sharp acceleration, induced by alkoxide ions, of the decomposition of 3-hydroxypropylphosphonium chloride (CX) (the rate constant at 60 °C is 7.3 litre mol^{-2} min^{-1}), compared with triphenyl-n-propylphosphonium chloride (the rate constant at 60 °C is 0.003 litre mol^{-2} min^{-1}):[114,115]



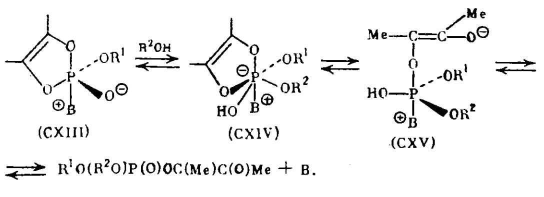
It has been suggested that tetracoordinate phosphorus compounds can give rise to P(VI) intermediates in chemical reactions involving base-catalysed nucleophilic substitution at a tetrahedral phosphorus atom.

In the presence of bases, the cyclic enediol phosphates (CXI) readily phosphorylate alcohols to form asymmetric diesters of phosphoric acid.[41,116] Effective catalysis by bases (amines,[117,118] phenoxides,[119,120] and the acetate ion[121]), which increases the rate of reaction by tens and hundreds of times, takes place in these reactions:



The mechanism of the catalytic action of bases is associated with the formation in the first stage of the hydroxyphosphorane (CXIII), which is obtained either by the reaction of the full phosphates (CXII, X = OR) with the catalyst or as a result of the addition of the alcohol to the enediol phosphate with a P–N bond (CXII, X=N, Netc.).[116]

The interaction with the substrate leads to an increase of the coordination number of the phosphorus atom in the rapidly formed intermediate phosphorate (CXIV):



The removal of one of the ligands in the intermediate (CXIV) converts the latter into the phosphorane (CXV) and then into the reaction products.

The essential feature of the catalytic action of bases apparently consists in increasing the rate of addition of nucleophiles to a phosphorane intermediate of type (CXIII) compared with the rate of reaction with the initial phosphate.

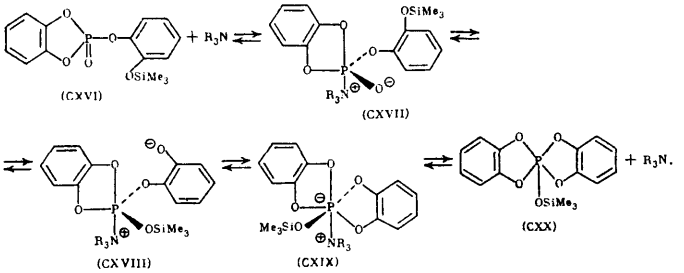
The phosphorylation of enediol phosphates by amide derivatives is accompanied by autocatalysis, because the interaction of, for example, the phosphimidazole (CXII, X = imidazolyl) with alcohol in the first stage is associated with the liberation of imidazole, which ensures effective catalysis of the phosphorylation reaction.[116–118,122]

The duration of the reaction of phosphoric acid triesters in the presence of imidazole is 2–30 min, while in its absence it is 8–12 h.[117] Triethylamine is just as effective in the reactions of primary alcohols and hardly affects the rate of phosphorylation of secondary alcohols. This is caused by the high steric requirements by the tertiary amine under the conditions involving the formation of a hexacoordinate intermediate. A definite role is also played by the basicity of the amine. Thus, in the base-catalysed opening of the ring in enediol phosphates by alcohols, the effectiveness of the catalysis is correlated with the basicity of the amines.[123]

The catalytic action of the *p*-nitrophenoxide ion in the trans-esterification of *p*-nitrophenyl diphenyl phosphate by alcohols has been explained by the formation of acyclic P(VI) intermediates.[116,124]

It has been noted[117,119] that the mechanism discussed here probably operates in the action of enzymes catalysing the reactions of phosphates and pyrophosphates in biological systems, because the presence of tyrosine, lysine, arginine, and histidine facilitates the addition of nucleophiles to a tetracoordinate phosphorus atom.

The base-catalysed cyclisation reactions of tetracoordinate phosphorus compounds containing an ω-hydroxyalkyl, *o*-hydroxy, or *o*-siloxyphenyl group [11,12] also take place with participation of P(VI) intermediates. Thus silyl transfer, which is responsible for the occurrence of the phosphate–phosphorane equilibrium (CXVI) (CXX), is accelerated by amines, the effectiveness of such catalysts diminishing as the steric requirements of the amines become more stringent.[125] The process includes the addition of the amine to the phosphate with formation of the monocyclic phosphorane (CXVII), in which the trimethylsilyl group is transferred from the phenoxy-oxygen to the equatorial oxy-anionic centre, so that the intermediate phosphorane (CXVIII) is produced. The addition of the anion to the phosphorane centre leads to the spirobicyclic zwitter-ionic phosphorate (CXIX), whose decomposition to the amine and siloxyphosphorane completes the isomerisation process:



The examples of the base catalysis of nucleophilic reactions of tetracoordinate phosphorus compounds presuppose the occurrence of two successive stages involving the addition of nucleophilic species to the tetrahedral phosphorus atom of the substrate and the phosphorane centre of the intermediate, which necessitates the participation of intermediates with the phosphorate structure in these processes. In this connection we may note that the formation of P(VI) intermediates, which may arise by the reaction of two hydroxide ions with the phosphoryl centre, has not been ruled out in the hydrolysis of five-membered cyclic phosphates either.[126,127] This hypothesis has been based on the experimental observation of a second-order dependence on hydroxide ion at high pH (in excess of 10) on the hydrolytic reaction.

However, the attempts to demonstrate the formation of phosphorate intermediates in the hydrolysis of ethyl ethylene phosphate using an isotope label and ^{31}P NMR (190.3 MHz) were not successful.[128] Nevertheless, the experimental data presented in this section make it necessary to consider the possibility of the formation of P(VI) structures and processes involving the interaction of tetracoordinate and even more so pentacoordinate phosphorus compounds with nucleophilies.[129] Furthermore, the data obtained in recent years leave no doubt that intermediates containing a P(VI) atom do in fact to a large extent determine the kinetic and synthetic results in many reactions of phosphoranes.[12]

It is known[12] that nucleophilic substitution at a pentacoordinate phosphorus atom can proceed via one or two mechanisms—dissociative, presupposing the unimolecular decomposition of the phosphorane to a phosphonium intermediate, and associative, in which nucleophilic species are added to or eliminated from the P(V) atom of the substrate. the formation of P(VI) intermediates in the second case has been established experimentally by isolating the products of the addition of ionic or neutral nucleophiles to phosphoranes.

Theoretical calculation for the minimum reaction energy pathway (MREP) in nucleophilic substitution at the P(V) involving the simple model reactions (2)–(4), i.e.

$$H^{\ominus} + PH_5 \rightleftarrows (PH_6)^{\ominus} \rightleftarrows PH_5 + H^{\ominus}, \tag{2}$$

$$H^{\ominus} + PH_4Me \rightleftarrows (PH_5Me)^{\ominus} \rightleftarrows PH_4Me + H^{\ominus}, \tag{3}$$

$$H^{\ominus} + PH_3Me_2 \rightleftarrows (PH_4Me_2)^{\ominus} \rightleftarrows PH_3Me_2 + H^{\ominus}, \tag{4}$$

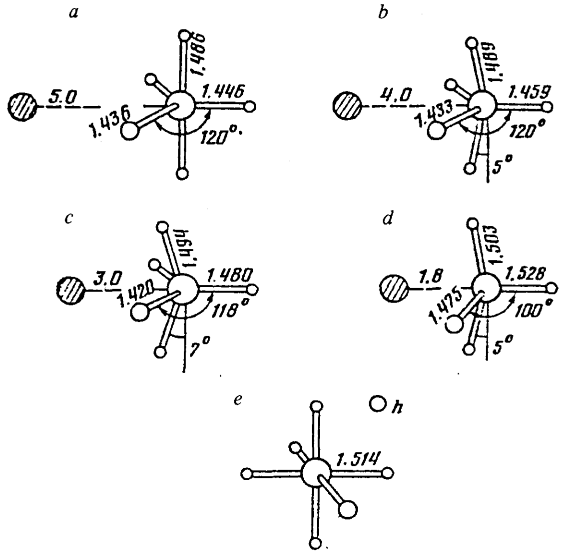
demonstrated that the attack by the hydride ion takes place rigorously in the equatorial plane of the trigonal bipyramid of the substrate.[95] The interaction leads to an octahedral intermediate and the main geometrical rearrangement of the system takes place in the reaction zone ($R \cong 2.0–2.2$ Å) with a gradual decrease of the total energy (see Figure). The *trans*-equatorial ligand begins to "sense" the approach of the nucleophile even over long distances and the *trans*-P–H bond gradually lengthens and, when the interaction is completed, reaches its equilibrium value. The lengths of the *cis*-P–H bonds increase monotonically.

Calculations for the less symmetrical RR^1PH_3 molecules have shown that the energetically most favourable direction of attack of a nucleophile involves movement along the bisector of the RPR^1 angle.

According to the data of Minaev and Minkin,[95] the addition of the nucleophile to the P(V) atom results in the preferential *cis*-disposition of the most electronegative group and the removal of the electronegative group being substituted takes place in the *cis*-conformation. #

The view has been expressed recently that equatorial attack by the nucleophile in the trigonal bipyramid of the phosphorane intermediate[130] and not only axial attack, as had been believed previously,[11] is possible also in reactions involving nucleophilic substitution at a tetrahedral phosphorus atom proceeding with retention of configuration.

At the same time, it has been shown[46,48] that, when the formation of P(VI) anions is subject to kinetic control, the addition of ionic nucleophiles to spirophosphoranes results in the initial formation of *trans*-phosphorates, which isomerise on raising the temperature to the thermodynamically favourable *cis*-phosphorates[12] (see also Section IV).



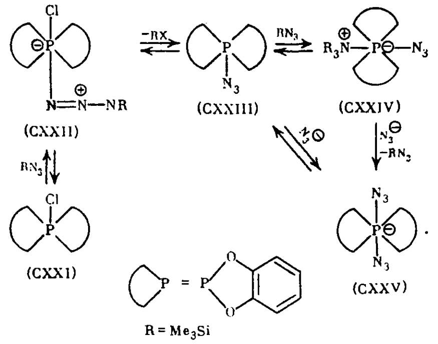
The minimum energy pathway in reaction (2);[95] the heats of formation of the supermolecule (ΔH_f, kcal mol^{-1}) are quoted for different distances R between the hydride ion and the attacked molecule: *a*) 120.5; *b*) 118.4; *c*) 115.4; *d*) 88.9; *e*) 78.6.

The formation of phosphorate intermediates in nucleophilic substitution at a pentacoordinate phosphorus atom has been detected in many instances by NMR.[12]

In the reaction of the chlorophosphorane (CXXI) with trimethylsilyl azide at −100 °C, the main product is the zwitter-ionic adduct (CXXII), which eliminates chlorotrimethylsilane at −60 °C and is converted into the azidophosphorane (CXXIII). However, the use of a twofold excess of the silyl azide yields as the main component of the reaction mixture the phosphorate (CXXIV), which is subsequently converted into compound (CXXV) (Scheme 5).

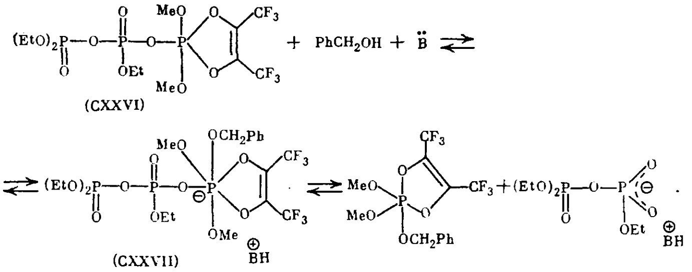
The equilibria (CXXIII) $\rightleftharpoons$ (CXXIV) and (CXXIV) $\rightleftharpoons$ (CXXV) are characteristic of the interaction of phosphoranes with nitrogen-containing nucleophiles (see Section IV). Phenylenedioxytrichlorophosphorane also combines with the azide molecule in the first stage and then exchanges in succession all the chlorine atoms for the azido-ligands

Scheme 5

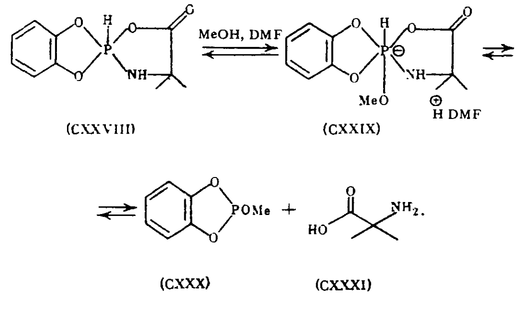


Thus reactions involving the nucleophilic substitution of chlorine atoms by azide ions proceed via a series of consecutively formed individual phosphorate intermediates.[131]

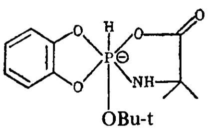
The interaction of hydroxyphosphoranes with alcohols, which takes place via transesterification[41,132,133] or alcoholysis[55] mechanisms, also involves the intermediate formation of phosphorates. Thus in the presence of γ-collidine, benzyl alcohol substitutes the pyrophosphate ligand in the phosphorane (CXXVI) in a relatively rapid and reversible reaction proceeding via the monocyclic phosphorate (CXXVII). The coordination of the phosphorus atoms is preserved in the reaction products.[41]



However, in alcoholysis reactions leading to products with a reduced coordination number of the phosphorus atom, the formation of phosphorate intermediates can be established spectroscopically in many instances.[55] The methanolysis of the hydrophosphorane (CXXVIII) in DMF leads to the cyclic phosphite (CXXX) and the aminoacid (CXXXI). At −60 °C a high-field signal [δ(^{31}P) = 110 p.p.m., $J_{\rm PH}$ = 760 Hz] was recorded in the NMR spectrum of the reaction mixture:



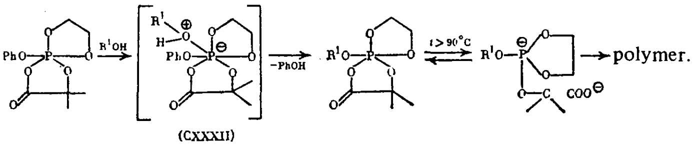
The signal was assigned to the intermediate (CXXIX) on the basis of a comparison with the similar spectroscopic characteristics of the phosphorate (CXXXII) obtained from compound (CXXVIII) and t-BuOK.



(CXXII) δ(^{31}P) = −112 p.p.m., J_{PH} = 740 Hz

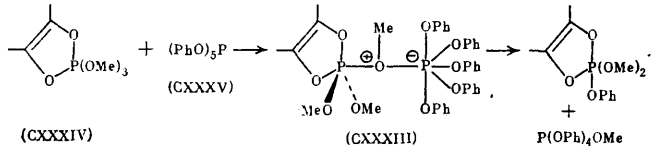
It is striking that the attack by the nucleophile is directed not to the alternative electrophilic centre of the molecule of compound (CXXVIII), namely the carbonyl carbon atom, but to the phosphorane phosphorus atom, which is known[12] to be characterised by a pronounced Lewis acidity. The replacement of the phenylenedioxy-substituent in compound (CXXVIII) by the less electron accepting ethylenedioxy-group precludes the detection of the P(VI) intermediate in the course of alcoholysis.[55]

It has been suggested that the transesterification of spirophosphoranes in neutral media and their subsequent polymerisation at an elevated temperature (>90 °C) proceed via a stage in which bicyclophosphorates (CXXXII) are formed:[134]



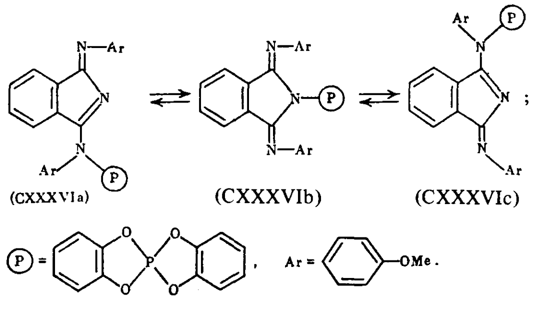
(CXXXII)

The formation of the oxonia-phosphorate intermediate (CXXXIII) probably ensures[135] intermolecular ligand exchange between the cyclic and acyclic phosphoranes (CXXXIV) and (CXXXV):



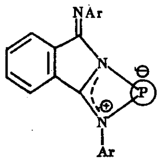
(CXXXIV) (CXXXIII)

Systems in which phosphotropic tautomerism occurs with participation of the phosphoranyl group have been discovered recently.[136] Two equal intensity singlets, at 3.63 p.p.m. (1) and 3.94 p.p.m. (2), as well as a singlet at 3.75 p.p.m. (3) with the intensity ratio (1 + 2) : (3) = 0.45 : 0.55, have been observed in the ^{1}H NMR spectrum of a solution of the phosphorane (CXXXVI) in o-dichlorobenzene at 25 ° C. The ^{31}P NMR spectra also contain two singlets with δ(^{31}P) = −26.8 and −36.7 p.p.m. and the same intensity ratio. The proton signals coalesce at 120 °C. This spectral pattern was explained by the existence of a dynamic equilibrium between the forms (CXXXVIa), (CXXXVIb), and (CXXXVIc) owing to two consecutive 1,3-migrations of the phosphoranyl group in the N=C–N=C–N pentad of compound (CXXXVI):



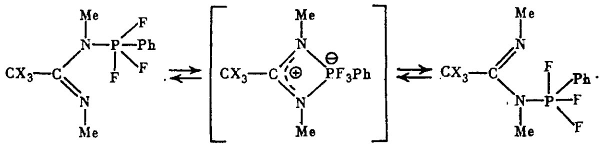
(CXXXVIa) (CXXXVIb) (CXXXVIc)

The free energy of activation for the process is 16.9 kcal mol^{-1}. The rate of these migrations is independent of concentration, which indicates an intramolecular mechanism of this phosphotropic process, involving the formation of the intermediate (CXXXVII) with a hexacoordinate phosphorus atom, which is short-lived on the NMR time scale and cannot therefore be detected spectroscopically.

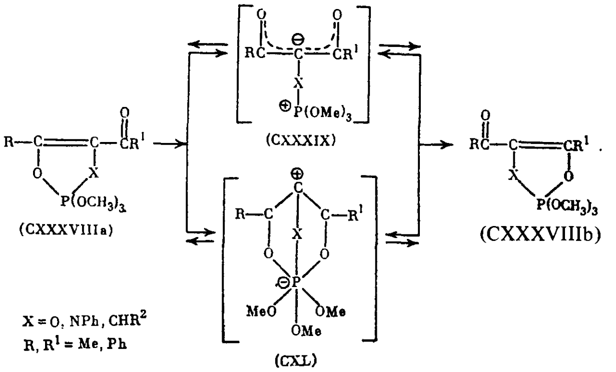


(CXXXVII)

A degenerate triad phosphotropism, associated with the migration of the PF_3Ph group, occurs in the phosphorane derivatives of trihalogenoacetamidinium. The intermediate phosphorate intermediate cannot be detected, because it is destabilised by the electron-accepting group at the cationoid carbon atom and the phenyl group at the phosphorate phosphorus atom:[137]



One cannot rule out the possibility that the phosphorotropic tautomerism (CXXXVIIIa) ⇌ (CXXXVIIIb), observed in monocyclic phosphoranes containing an acyl group at an endocyclic carbon atom,[138-140] can involve not only a dissociative mechanism via a betain intermediate (CXXXIX) with the phosphonium atom, but also via an associative mechanism with participation of a hexacoordinate intermediate or transition state (CXL). However, the experimental data are insufficient to make a choice between these variants.



(CXXXVIIIa) (CXXXIX) (CXXXVIIIb) (CXL)

X = O, NPh, CHR^2
R, R^1 = Me, Ph

The present paper completes a series of reviews[10-12] devoted to the chemistry, mainly reactivity, of 1,3,2-diheterophosphacyclanes containing a phosphorus atom with different coordination numbers. Summarising briefly the literature data of the last decade, one must note that all the main current trends in the development of organophosphorus chemistry have been reflected in the chemistry of these phosphorus-containing heterocycles. The endeavour by investigators to establish a relation between the structure and reactivity of OPC and to express it quantitatively whenever possible must be included among them in the first place. Much attention has been devoted to the study of the fine details of the reaction mechanisms and through their understanding to the development of new methods of synthesis of OPC, including those which are practically useful. The discovery of the character and role of the intermediates in the reactions of OPC is important for the development of the chemistry of phosphorus compounds at the present stage. It has led investigators to recognising the fact of the relative ease with which the coordination number of the phosphorus atom can change and to new views on the character of the driving forces in the reactions of OPC and has strongly stimulated progress in the chemistry of hypervalent compounds of phosphorus and other non-transition elements.

At the same time, many problems in the chemistry of 1,3,2-diheterophosphacyclanes, such as the character of the intramolecular electronic interactions, the manifestation of the stereochemistry of the phosphorus-containing heterocycle in the reactivity of OPC of this type, the quantitative characteristics of the electronic and steric effects of the alkylene(phenylene)dihetero-substituent or the entire phosphacyclane fragment, and many others still require a more far-reaching development. We are confident that studies in the near future will be marked by new successes in this rapidly developing field of organophosphorus chemistry.

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The Resonance Raman Light Scattering in Studies of the Structures and Functions of Flavins and Flavoproteins

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The application of the spontaneous and non-linear resonance Raman spectroscopic methods in studies on flavins and flavoproteins is examined. The biological functions of flavin systems are briefly surveyed and the parameters of the resonance Raman spectra and their relation with the electronic structure of the isoalloxazine ring in various oxidation states are described. The possibilities of identifying the flavin chromophore in a protein environment, in charge-transfer complexes, and in modified systems are discussed.

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I. THE LINEAR AND NON-LINEAR RESONANCE RAMAN SPECTROSCOPIC METHODS

Resonance Raman light scattering (RRS) was observed in the 1950's before the appearance of universal Raman scattering (RS) excitation sources—lasers. "Resonance" implies in this sense the coincidence of the frequency of the exciting light with one of the frequencies of the electronic transition in the molecule. This term was first applied to the description of the large increase in the intensities of certain Raman lines of aromatic nitro-compounds on excitation in the long-wavelength absorption band region.[1] All the characteristic features of RRS were described in subsequent studies:[2-4] high intensity coefficients exceeding by a factor of 10^3-10^9 the intensity of the usual RS; selective intensification of only certain normal vibrations among those actually applicable to the given electronic absorption band; the appearance in certain cases in the Raman spectrum of progressions of intense overtones; relations between the RRS line intensities and the parameters of the electronically excited state. These properties made it possible to expand greatly our ideas about the interaction of light with matter and to obtain new information about molecular structure and have led to analytical possibilities unavailable in the traditional RS methods. The invention and theoretical application towards the end of the 1960's of lasers led to a vigorous growth of the applications of RS, in particular RRS, in the solution of a wide variety of problems in physics, chemistry, and biology.[5,6] At the same time numerous non-linear effects, arising in matter under the influence of coherent laser beams, were observed and foundations were laid for a new field—non-linear optics and one of its branches, namely non-linear scattering spectroscopy.

In contrast to the traditional spontaneous RS, arising from fluctuation (thermal) vibrations, in non-linear scattering spectroscopy one considers the interactions with forced intramolecular vibrations which are excited under certain conditions by the powerful light fields of lasers in a large volume of matter. It is important to emphasise that the coincidence of the phases (phase synchronisation) of the forced vibrations plays the main role in these processes, whereas their amplitudes in the strongest light field remain smaller by 2–3 orders of magnitude than the fluctuation (spontaneous) changes in the normal nuclear coordinates. The first of these phenomena observed was forced Raman scattering (FRS).[7] Although the spectroscopic possibilities of this method are extremely limited, it served as the physical foundation of a whole series of non-linear Raman spectroscopic methods developed in the subsequent decade[8] and based on measurements of the amplitude, polarisation and phase of coherent waves "scattered" by forced vibrations.[9,10] Although many of these processes are not scattering in the traditional sense of the word, their interpretation may be based on classical ideas about the modulation of polarisability by normal nuclear vibrations, which are widely used in spontaneous Raman spectroscopy and which only arose at the time of the publication of Placzek's book,[11] while the parameters of the non-linear scattering—the intensities, forms, half-widths, and positions of the signal—may be compared with spontaneous RS data.

The rapid progress in the technology of lasers with tunable frequencies resulted in what were initially unique measurements becoming routine measurements.[12] Two non-linear Raman spectroscopic methods, which have found most practical applications and whose variants analogous to spontaneous RRS have also been investigated, are briefly described below.

The Coherent Anti-Stokes (Stokes) Light Scattering (CALS and CSLS) Spectroscopy. Two coherent beams with the frequencies ω_1 and ω_2 such that their difference $\omega_1-\omega_2$ coincides with one of the intramolecular vibration frequencies ω_r can be excited and phase-synchronised against the background of the vibration with the frequency ω_r; a third (trial) wave then interacts with forced vibrations, is scattered, and gives rise to intense coherent components in the anti-Stokes and Stokes regions:[8]

$$\omega_{a,\,c}=\omega\pm(\omega_1-\omega_2)\quad .$$

The most widely used version of this method is one where one of the pumping waves is used as the trial wave ($\omega = \omega_1$):

$$\omega_a=2\omega_1-\omega_2\quad ,$$

Evidently, by varying the difference $\omega_1-\omega_2$, it is possible to obtain all the frequencies corresponding to the spontaneous Raman spectrum of the molecule. The abbreviations CALS and CSLS widely used nowadays in the foreign literature were introduced by Byer et al;[13] however, even earlier Akhmanov and co-workers[10] proposed for this process the term "active RS spectroscopy (ARSS) which we shall also use subsequently.

The analogue of spontaneous RRS, where the coherent pumping frequency ω_1 is close to the frequency of the electronic (one-photon) transition in the molecule ω_e, is nowadays vigorously investigated in the CALS spectroscopy. On decrease of the difference $\omega_1-\omega_e$, a sharp increase in the intensity of the coherent signal was observed in the CALS spectra.[14,15] In the region of the one-photon resonance, the CALS and CSLS lines have extremely complex contours due to the interference of several contributions—electronic and vibrational (see, for example, Refs.9 and 10). This factor initially led to an erroneous interpretation of the observed phenomenon as inverse RS[15] (see below). Theoretical analysis within the framework of quantum-mechanical ideas has shown[16] that, when ω_1 is scanned in the region of a broad electronic absorption band, the contour of the anti-Stokes line can vary from positive Lorentzian through dispersion to negative Lorentzian, depending on the ratio of the parameters: the frequencies ω_1, ω_e, and ω_r and the decay constants Γ_e and Γ_r of the electronic and vibrational oscillators. For identical values of $\omega_1-\omega_e$, the CALS and CSLS signals have different forms (Fig.1). This has been observed experimentally for cytochrome c,[15] vitamin B_{12},[15] β-carotene,[17] and certain other biologically active substances.[9]

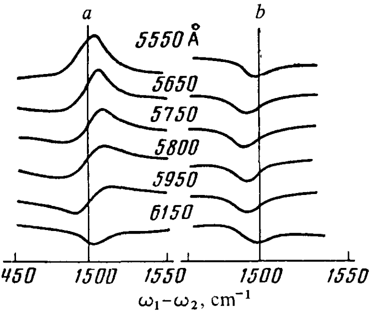

Figure 1. A model calculation of the CALS (*a*) and CSLS (*b*) band contours on resonance excitation;[16] the values of the parameters simulate the case of vitamin B_{12}; ω_e = 18,000 cm^{-1}, ω_r = 1500 cm^{-1}, Γ_e = 500, and Γ_r = 10.

Inverse Raman Spectroscopy. CALS and CSLS are four-photon processes. A lower-order non-linear process, namely a two-photon process, was also observed in the 1960's. When two coherent beams with the frequencies ω_1 (intense pumping) and ω_2 (weaker trial wave) were allowed to interact with the medium, Jones and Stoicheff[18] observed a weakening of the intensity of the trial wave, while the frequency difference $\omega_2-\omega_1$ coincided with the vibrational transition frequency ω_r:

$$\omega_2-\omega_1\simeq\omega_r;\quad \omega_1<\omega_2$$

This phenomenon was called the inverse Raman effect.[18] Instead of the weakening of the trial high-frequency wave in the field of powerful low-frequency pumping, one can employ another scheme and observe an intensification of the trial low-frequency ω_2 wave under the influence of the intense high-frequency ω_1 pumping.[19] The corresponding terms have been proposed in the Soviet literature: forced RS (FRS) in intensification and inverse RS (IRS) in attenuation.[10] These methods are sometimes referred to as modulation methods bearing in mind the change in the optical properties of the medium at the frequency of the trial wave.[10]

The case of "double resonance", vibrational and electronic (one-photon), has also been investigated in inverse Raman spectroscopy. This method has a number of advantages, among which the absence of an intense permanent background, associated with the non-resonance electronic susceptibility and generating a serious interference in the CALS and CSLS spectra (under conditions remote from one-photon resonance), is important.[9,10] It has also been suggested that, in contrast to ARSS, in the intensification–attenuation scheme it is possible to obtain spectra fully corresponding to spontaneous RS, including the form of the signal.[19,20] In the first experiment on resonance inverse RS, direct measurements were made of the absorption.[21] Subsequently various modulation schemes were proposed[22,23] permitting a significant improvement of the detection limits.[24] The experiments on the excitation of inverse RS in the region of broad electronic absorption bands showed that[24] the form of the signal changes as a function of the ratios of ω_1, ω_e, and Γ_e. The results of a model parametric calculation of the resonance inverse RS line contour are presented in Fig.2.

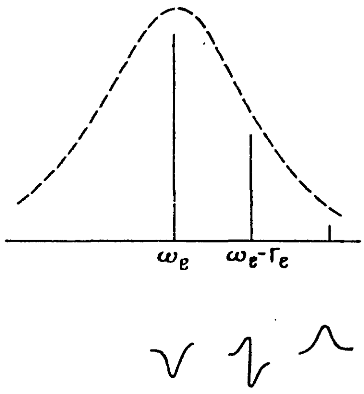

Figure 2. The contours of the inverse Raman signal (below) on excitation in the region of the absorption band (shown dashed); model calculation.[24]

The advantages of coherent Raman spectroscopy in the study of rarefied gases and in the diagnostics of plasma, rapid combustion processes, etc. have been frequently noted.[8,10,12] In comparing the possibilities of spontaneous RRS and its coherent analogues in studies of the structures of complex molecules in condensed phases, one should note in the first place the difficulties associated with the extraction of information from coherent Raman spectra in the region of one-photon resonance; the treatment of spontaneous RRS data is in this case much simpler. The ARSS and inverse Raman spectra have been calculated on a computer by adjusting parameters. At the same time, the complexity of the form of the coherent signal and the changes in the latter in the resonance region due to the interference by several contributions make it possible to obtain, with the aid of parametric analysis, a series of additional data—in particular one can estimate the decay constants for the electronic and vibrational oscillators, determine the frequencies in the excited state of the molecule, and refine the position of the 0–0 transition. However, all these processes have so far been inadequately studied.

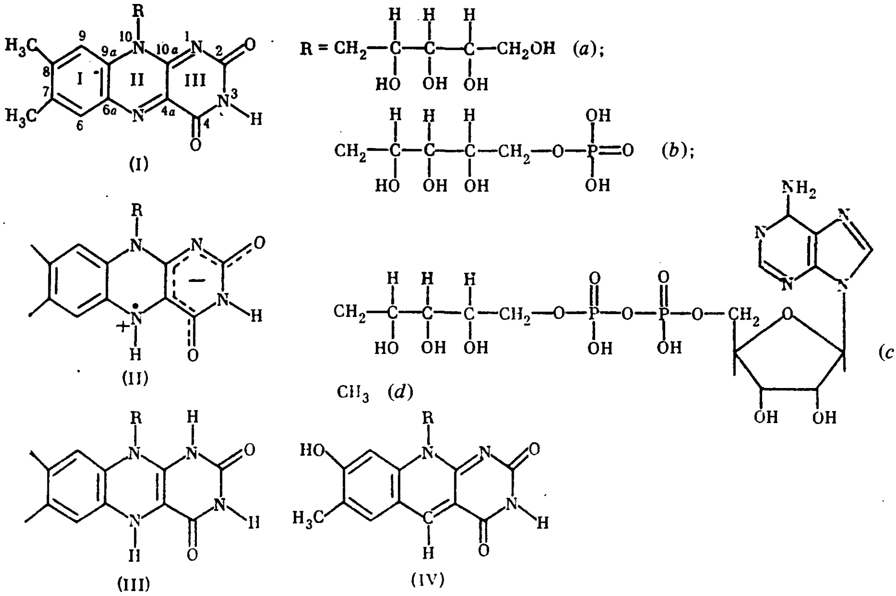

Figure 3. The prosthetic flavin groups and the numbering of the atoms in the isoalloxazine ring (I): *a*) riboflavin; *b*) flavin mononucleotide; *c*) flavin adenine dinucleotide; *d*) lumiflavin; II) semiquinone form; III) fully reduced form; IV) 5-deaza-8-hydroxyflavin.

The excitation in the region of resonance of complex and especially biological molecules is known to entail frequently the appearance of an intense fluorescence, which fully rules out the observation of spontaneous RRS. Since the CALS and inverse Raman signals are located in the anti-Stokes region and the fluorescence occurs in the Stokes region, they provide a unique possibility for recording Raman spectra in the presence of fluorescence. We may also note that the average level of the intensity of the irradiation of the specimen in the coherent spectroscopy is lower by 1–2 orders of magnitude than in the recording of spontaneous Raman spectra, which is important for photolabile substances.

Thus non-linear Raman spectroscopic methods significantly supplement the spontaneous spectroscopic method and sometimes constitute the only means of observing the Raman spectra. Yet another field, associated with studies on non-stationary processes and the determination of the dynamic characteristics of short-lived intermediate states, which is extremely important for biology, has developed rapidly during the last decade within the framework of non-linear spectroscopy (see, for example, Akhmanov and Koroteev,[10] Chapter 5). Progress in the technique of the generation of short and ultrashort [picosecond (10^{-12} s)] pulses and the creation of adequate recording methods[25–27] permitted the study of rapid biological processes, including the conformational rearrangements in the active centres of haemoproteins[28] and in visual pigments.[29]

The scale reached by studies with the aid of linear and non-linear resonance Raman spectroscopy in biology can be inferred from the appearance of the term "resonance Raman spectroscopy of haemoproteins",[30] "resonance Raman spectroscopy of visual pigments",[31] etc. The comparatively new rapidly developing field of flavoproteins has been least thoroughly investigated in this sense.[32–34] This review discusses resonance Raman spectroscopic data obtained for flavin and flavoproteins in connection with their structures and functions; the latest ideas concerning the role of flavoproteins in living nature and certain mechanisms of their action are also briefly surveyed.

II. THE STRUCTURES AND FUNCTIONS OF FLAVOPROTEINS

Flavins and Flavoproteins. This important class of natural products has been little investigated partly because of historical reasons† as well as a number of other factors: the great complexity of the molecules, the difficulty of isolation, the low content in natural objects, and, which is most important, the unusual wide variety of the functions of flavin-containing compounds in nature: in higher animal and plant organisms as well as micro-organisms. Flavoproteins are in most cases enzymes with a prosthetic group containing a substituted isoalloxazine ring (Fig.3), usually in the form of flavin mononucleotide (FMN), flavin adenine dinucleotide (FAD), or riboflavin. The highly conjugated tricyclic isoalloxazine system, in which there are comprehensive possibilities for electronic rearrangement by virtue of the presence of four nitrogen atoms and fragments analogous to the amide group, constitutes the centre of numerous biochemical reactions. The flavin system incorporated in a wide variety of protein environments—from comparatively short polypeptide chains (flavodoxins, ~130–170 aminoacid residues[35]) to enormous dimeric molecules (glutathione reductase, ~480 residues in each subunit[36,37])—affects the enzyme catalysis of the oxidation-reduction reactions of an enormous number of substrates, including amines, alcohols, amino- and hydroxy-acids, dithiols, etc.[34] The reactions of flavoproteins with molecular oxygen are no less varied. In certain oxidative processes, one oxygen atom of the O_2 molecule is transferred to the substrate, while the other is incorporated in a water molecule; in other reactions, molecular oxygen is reduced with formation of the superoxide O_2^-.

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†The first natural flavin compound, namely riboflavin, was identified in 1935, while the most important prosthetic group, flavin adenine dinucleotide, was not identified until 1954.

Apart from its life supporting functions in organisms and plants, flavin enzymes play an enormous role in the turnover of the elements in nature effected by micro-organisms, in particular in the global turnover of carbon.[38] In the course of evolution, soil bacteria developed a wide variety of enzymes (monoxidases) catalysing the decomposition of residues from higher plants, mainly lignin, which is a stable natural polymer.[38] The function of flavin enzymes is just as important in the metabolism of nitrogen and especially sulphur, whose biological circulation effected by bacteria has been estimated[39] as amounting to 75% of the total content of sulphur on earth.

The applications of these compounds have extensive biomedical aspects. In the organisms of higher animals, the most important agent supporting the normal level of flavoproteins is riboflavin, which is ingested with food and is then transferred by special transfer proteins to the tissues, where it is bound in the form of FMN and FAD cofactors to other proteins.[40] One can apparently expect that in the immediate future it may be possible to approach an understanding of certain molecular aspects of diseases (including certain hereditary afflictions of the brain and the peripheral nervous system) associated with the deficiency of flavoproteins and the disturbance of their metabolism in the organism.[41] This is also indicated by the development of the medicinal antihypertensive agents and psychotropic preparations (derivatives of phenothiazine and tricyclic antidepressants), whose structure is close to that of riboflavin; their activity is apparently based on the inhibition of the conversion of riboflavin into FMN and FAD in the organism.[42] The functions of flavoproteins determining the occurrence of various detoxification processes, involving a wide variety of aromatic compounds, sulphur-containing derivatives, and mercury, have also been elucidated.

The multiplicity of functions of flavin enzymes has become evident only recently. On the basis of mainly biochemical data which have now accumulated, Massey and Hemmerich[43] suggested that five main classes of flavoprotein can be distinguished in accordance with the characteristic features of their catalytic cycles.

The field of flavins and flavoproteins is developing rapidly. Unusual flavin enzyme systems containing a modified isoalloxazine ring, including flavins with "double modification" of the ring—the 5-deaza-8-hydroxy-derivative (Fig.3), the so-called F-420 cofactor of methane bacteria, have been discovered and investigated.[44,45] In contrast to haemoproteins, the flavin group does not form covalent bonds with the protein in most cases and is retained in the active centre mainly with the aid of strong hydrogen bonds, favourable electrostatic interactions, etc. However, whole series of flavoproteins have now been identified in which the isoalloxazine ring proved to be covalently bound to the apoprotein, usually in the C(8)-position via a CH_2 group to histidine, cysteine, or tyrosine residues.[46]

Nevertheless, despite the undoubted progress made, the field of flavoproteins has so far been developing mainly via the extensive accumulation of new data, leaving many problems unsolved. The true natural substrates are unknown for a whole series of flavoproteins distributed in animal and plant tissues; the biological functions of many flavoproteins, including one of the first compounds identified—"the old yellow enzyme", have not been elucidated either. The biological role of the covalent bond between the isoalloxazine chromophore and the protein in covalently bound flavoproteins is unknown. All the biological oxidation-reduction chains contain at least one flavoprotein, which transforms two-electron transport into one-electron transport to a "one-electron" acceptor (cytochrome or sulphur-containing protein). The unique mechanism on this $2e^-/1e^-$ switch still remains obscure.

Protein plays an enormous role in the functioning of flavin enzymes. The immediate protein environment of the isoalloxazine ring actually determines ultimately its specific function in the enzyme. However, our information about this field is still very limited and the structure (even the primary structure) of many vitally important flavoproteins remains unknown. X-Ray diffraction data have now been obtained for representatives of only three classes of flavoproteins: flavodoxins,[47] glutathione reductases,[36] and p-hydroxybenzoate hydroxylases.[48] Furthermore, it is evident that only knowledge of the details of the steric structure of the active centre (in certain cases even the static [resting-state] structure) would make it possible to reach well-founded conclusions about the mechanism of the catalysis and the character of the intermediate stages. The example of glutathione reductase is instructive from this point of view; according to X-ray diffraction data,[36,37] the immediate environment of FAD in this enzyme predetermines its functions as a two-electron transferring agent and blocks the structures necessary for the transfer of one electron. However, this example is exceptional and most of the proposed mechanisms of the biochemical reactions of flavoproteins remain extremely speculative. In order to account for the mechanism and to identify the intermediate stages, traditional biochemical methods are resorted to, in particular methods using the formation of artificial complexes of the enzyme with the inhibitors. Another procedure for the "probing" of the active centre is based on the ease of the separation of the flavin chromophore from the aproprotein,[49] which can then be joined to isoalloxazine chemically modified at points tentatively assumed to be of "key" importance for the kinetic and thermodynamic parameters of the catalysis. In order to deduce the environment of the isoalloxazine chromophore in the protein, indirect physical information is also used. For example, it is known that the intense fluorescence characteristic of flavins is quenched following addition to certain proteins. It has been suggested that this can occur only when the isoalloxazine ring interacts with the tyrosine and tryptophan in the active centres of the protein which are close to it in space.[35]

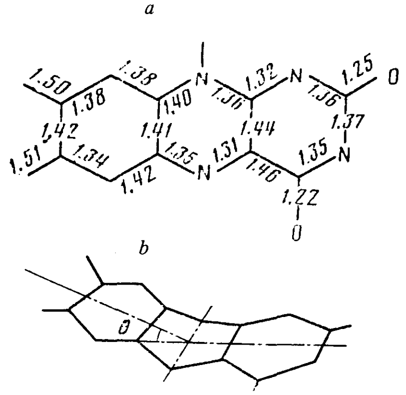

Figure 4. The bond lengths in the oxidised planar structure of the isoalloxazine ring (*a*) and the "butterfly" conformation of the fully reduced form (*b*); the energy minimum corresponds to the angle θ ≅ 15°.[50]

Electronic Absorption Spectra and Structural Parameters of the Isoalloxazine Ring. Three main biological functions of the isoalloxazine chromophore, namely (de)hydrogenation (only 2e$^-$), activation of molecular oxygen (2e$^-$ or 1e$^-$), and "pure" electron transport (1e$^-$), are possible by virtue of electronic rearrangements of three stable forms (Fig.3): oxidised, half-reduced (semiquinone; radical), and fully reduced. In addition various ionisation and protonation states are possible for the last two forms.

The structural parameters of the isoalloxazine ring are indicated in Fig.4. The conformational possibilities in the conjugated flavin system are extremely limited; according to X-ray diffraction data, the fully oxidised isoalloxazine ring in all the flavin systems investigated experimentally has a planar structure in conformity with the predictions of quantum-chemical calculations (see Dixon et al.[50] and the references quoted therein).

The "butterfly" conformation with a dihedral "folding" angle θ relative to the N(5)–N(10) axis of approximately 10° has been predicted for the fully reduced form by MO SCF calculations (in the INDO version—incomplete neglect of differential overlap)[50] (Fig.4). The experimental values of θ for this form in model systems vary in the range 30–8°, whereas in proteins the angle θ can apparently be even smaller.[51] Calculation has shown[50] that the variation of the angle θ in the range 20–0° can be achieved for an energy expenditure of approximately 3.5 kcal mol^{-1}, which corresponds to slight conformational rearrangements of the aminoacid residues in the protein surrounding the flavin. For this reason, a planar structure is apparently preferable for the semiquinone form in the protein environment.[52]

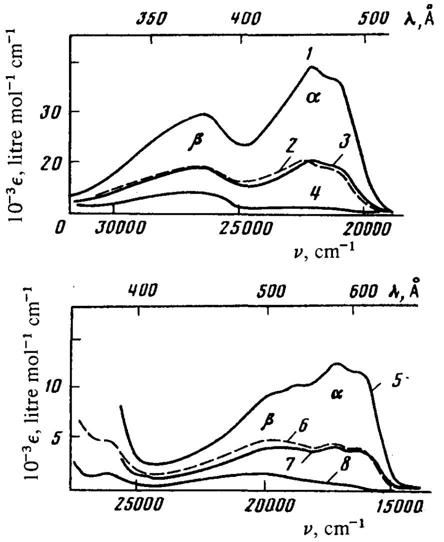

Figure 5. The electronic absorption spectra of an FMN-containing protein—flavodoxin from *Clostridium MP;* *a*) oxidised form; *b*) semiquinone form; the polarisation spectra of single crystals with $E \parallel$ crystal *c* axis (curves *1* and *5*) and $E_\perp$ crystal *c* axis (curves *4* and *8*) as well as the spectra of the solutions (curves *2* and *6*) are shown; curves *3* and *7* represent the calculated isotropic spectra of the crystals.[55]

The flavin chromophore has intense absorption bands in the long-wavelength part of the spectrum: one band at 20000–25000 cm^{-1} and another with centre at approximately 26400 cm^{-1},[53] which are due to the two lowest $\pi \rightarrow \pi^*$ transitions[54] and which will henceforth be designated as the α- and β-bands (Fig.5).[55] Polarisation measurements of the absorption in crystals[55] and earlier studies on oriented films and the polarisation of the fluorescence of model flavins showed that the corresponding transitions are linearly polarised in the plane of the flavin ring in the direction close to the axis parallel to the plane of the ring and perpendicular to the N(5)–N(10) axis.[55]

III. THE RESONANCE RAMAN SPECTROSCOPY OF FLAVINS AND FLAVOPROTEINS

The Non-Linear and Spontaneous Resonance Raman Spectroscopy of Flavins. The resonance Raman spectroscopy of flavin systems, like that of certain proteins of other classes, constitutes in essence the only (with the exception of X-ray diffraction analysis) source of the most detailed information about the structure of the active centre. Indeed, until recently, the electronic rearrangements of the isoalloxazine ring in the functioning of the flavoprotein could be inferred from only one parameter—the change in the positions and intensities of the long-wavelength $\pi \rightarrow \pi^*$ transitions.[43] Apart from the usual limitations, the application of NMR is in this case complicated also by the fact that, in addition to the protons of the two methyl groups in the 7- and 8-positions and the CH bonds in the 6- and 9-positions, whose signals contain little information, the isoalloxazine ring contains a single proton at the N(3) atom; the low relative content of the flavin fragment in proteins hinders the application of ^{13}C NMR. The NMR data obtained hitherto refer mainly to the ribityl fragment of FMN and FAD.[56]

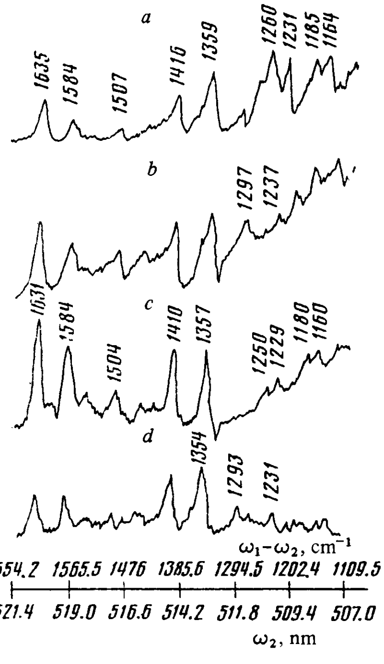

Figure 6. The resonance CALS spectra of flavin adenine dinucleotide [*a*) in H_2O; *b*) in D_2O] and riboflavin-binding protein [*c*) in H_2O; *d*) in D_2O]; pH 7; ω_1 = 480 nm.[58]

In a free state the flavin chromophore (FMN, riboflavin) exhibits a very intense fluorescence, its intensity exceeding by several orders of magnitude (by a factor of $\sim 10^4$) that of the Raman lines. The first resonance Raman spectra of FAD and FAD-containing protein (glucose oxidases) were obtained by means of the "spatial" separation of the scattering and fluorescence in the anti-Stokes ARSS (CALS) method with excitation in the region of the α-band.[57] The frequency $\omega_1 \cong 480.0$ nm, tentatively coinciding with that of the 0–0 transition (ω_{00}), was used as the pumping frequency.[54] Further improvement of the experimental technique (the introduction of a second monochromator into the optical path of the signal) made it possible to reduce the background in the vicinity of the pumping frequency and to obtain CALS resonance spectra for FAD and two FAD-containing proteins, glucose oxidase and riboflavin-binding protein (Fig.6), starting from 300 cm^{-1} in certain cases.[58]

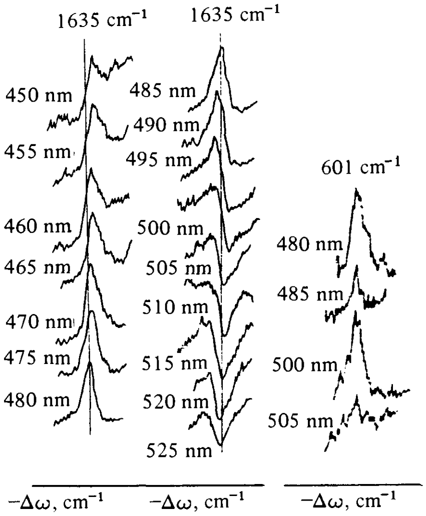

Figure 7. The $\omega_r \cong 1635$ and 601 cm^{-1} band contours in the resonance CALS spectra; the frequencies ω_1 are indicated in the Figure.[59]

As already mentioned, the major difficulties in the resonance excitation in the CALS are associated with the variation of the signal contour as a function of the ratios of ω_1, ω_e, ω_r, and a number of other parameters.[16] The FAD line contour ($\omega_r \cong 1635$ cm^{-1}) is illustrated in Fig.7 as a function of the varying ω_1 in the region of the α-band.[59] It is seen from these data that approximate estimates based on the semiclassical model[16,60] agree with experiment fairly satisfactorily (see also Fig.1). A positive Lorentzian contour is observed at $\omega_1 \cong \omega_0$; for higher and lower energies ($\omega_1 \cong \omega_{00} \pm \omega_{r/2}$), the signal becomes of the dispersion type and has a negative Lorentzian contour at $\omega_1 \cong \omega_{00} - \omega_r$.. We may note that, under the same excitation conditions, only a positive Lorentzian contour was observed for the $\omega_r \cong 601$ cm^{-1} lines, which the authors attributed to a large contribution of Franck–Condon factors.[59] In conformity with model calculations,[16] only dispersion line contours were observed for a coherent Stokes signal. Thus the exact determination of the frequency in the resonance CALS spectra may be difficult. The only practical procedure remaining so far is one involving the recording of a series of spectra at different pumping frequencies in order to discover the purely dispersion or purely Lorentzian contour.

Almost simultaneously with these studies, reports concerning the spontaneous resonance Raman spectra of flavins appeared. A group of Japanese workers[61]# used the ability, noted a long time ago, of the protein matrix to weaken greatly the fluorescence of the isoalloxazine chromophore and obtained the spectra of two riboflavin-binding proteins: from chicken egg yolk and white, and also of the 3-CH_3-, 2-CH_2COOH-, and 7,8-Cl-derivatives of riboflavin attached to the upper end of the apoprotein. Subsequently the resonance Raman spectra of several other flavoproteins and of the FMN and FAD prosthetic groups themselves were obtained; in order to eliminate the interfering fluorescent background, various procedures were employed; excitation by lines at longer wavelengths (600 nm; in the preresonance region)[63] or at shorter wavelengths (λ = 363.8, 351.1, 337.1, and 257.3 nm, in the region of high-energy electronic transitions of the chromophore), and also by adding quenching agents, mainly KI.[64,65]

In the first investigations,[57,58] it was already noted that only vibrations localised in the isoalloxazine ring are intensified by resonance and that, as might have been supposed, the vibrations associated with the substituents at N(10), namely ribose (in riboflavin), phosphoribose (in FMN), or adenosine diphosphate-ribose (in FAD), are not intensified. Typical FAD spectra are illustrated in Fig.6. We may note that some of the frequencies in the above study differ from those obtained subsequently in spontaneous Raman spectra (Table 1). Bearing in mind that positive CALS line contours are obtained at the pumping frequency $\omega_1 \cong 480$ nm[58] while negative contours are obtained at the frequency $\omega_1 \cong 495$ nm[66] the agreement between the frequencies in Table 1 can be regarded as satisfactory. It was shown subsequently that, under identical excitation conditions, the resonance Raman spectra of riboflavin, FMN, and FAD are almost identical in the region above 1100 cm^{-1} (for which reliable data are available) with the exception of small differences as regards the intensities of a number of bands.[64]

The Assignment of the Vibration Frequencies. In the very first studies, attempts were made to compare the resonance Raman frequencies with the structural elements of the isoalloxazine ring. The correlations were based initially on a single experiment involving isotope substitution [the replacement of the exchanging N(3)H proton by deuterium[58,61,63]] and also on data for 7,8-Cl-substituted derivatives[61] and intuitive guesses. However, a fundamental study by Kitagawa et al.,[67] who obtained the resonance Raman spectra for the N(3) and N(3)D forms of the isotope-substituted [2-^{13}C]-, [4a-^{13}C]-, [10a-^{13}C]-, [2,4,4a,10a-^{13}C]-, [5-^{15}N][1,3-^{15}N]- and [1,3,5-^{15}N]-riboflavins was soon published. In order to eliminate fluorescence, the authors used the ability of certain proteins, noted above, to exhibit a "quenching" effect on the fluorescence of isoalloxazine and the ease of the formation of its complexes with the apoprotein; the complexes of all the above derivatives with the riboflavin-binding protein from chicken egg protein were obtained in this way. The study of Kitagawa et al.[67] prepared a basis for a reliable calculation of the normal vibration frequencies of the flavin system, but these extremely rich data have remained virtually unused. The only calculation of the vibration spectrum of 10-methylisoalloxazine (lumiflavin) carried out hitherto[68] can be regarded as only preliminary.

#The observation of a single isoalloxazine line on excitation with a UV laser had been reported in an earlier study.[62]

Table 1. The frequencies of the resonance Raman lines of the prosthetic flavin groups (cm^{-1}).

Band designation	FAD (Ref.58)[a]		FAD (Ref.63)[b]		FAD (Ref.64)[c]	FMN (Ref.63)[c]		FMN (Ref.66)[d]		FMN (Ref.64)[e]
	H_2O	D_2O	H_2O	D_2O	H_2O	H_2O	D_2O	H_2O	D_2O	H_2O
I	1635 s	1634 s	1633 w	1628 w	1629	1633	1628	1629	1628	1626
II	1584 m	1584 m	1585 m	1584 m	1582	1584	1584	1582	1580	1583
III	—	—	1551 m	1548 m	1548	1551	1548	—	—	1549
IV	1507 w	1507 m	1504 m	1502 m	1500	1503	1502	1503	1504	1500
V	—	—	1468 w	1469 m	1461	1469	1468	—	—	1459
VI	1416 s	1416 s	1412 s	1410 s	1408	1413	1411	1412	1414	1405
VII	1359 s	1359 s	1356 vs	1351 vs	1353	1355	1351	1355	1357	1350
VIII	—	—	—	—	1280	—	—	—	—	1278
X	1260 m	1297 m	1261 m	1300 m	1255	1261	1300	1261	1300	1256
XI	—	—	1234 s	1233 m	1228	1233	1230	1233, 1192	—	1228
XII	1185 w	1179 w	1190 w	1171 m	1182	1187	1172	1170	—	1183
XIII	1164 w	1144 w	1166 m	1147 m	1160	1166	1149	1151	—	1158

[a] CALS, $\omega_1 = 480$ nm. [b] Spontaneous RS, $\lambda = 600$ nm. [c] pH 8.5 with added 5 M KI; spontaneous RS, $\lambda = 488$ nm. [d] In H_2O, CALS, $\omega_1 = 495$ nm. [e] In H_2O with added 6 M KI; spontaneous RS, $\lambda = 514.5$ nm. s = strong (intense), vs = very strong, m = moderate, and w = weak.

The force constants of the valence bonds and angles and also the interaction constants were in the main transferred in the above study from benzene, pyrimidine, and uracil molecules, taking into account the bond length—force constant correlations (see the references in the paper of Bowman and Spiro[68]). At first sight, the force field generated in this way could in principle reflect the specific features of the flavin system; the large bond interaction constants (up to 15% of the diagonal force constant) are characteristic of molecules with a high degree of delocalisation of the electron density. Nevertheless, almost all the frequencies calculated in terms of this approximation differ appreciably from the experimental values and in certain cases the differences for the most intensive bands reach 80–100 cm^{-1}. However, it is more significant that the calculated data do not reproduce the line shifts on isotope substitution.[67] This is particularly clear for the ~1250 and 1160 cm^{-1} bands, which undergo the greatest shifts on deuteriation, and in certain isotope-substituted specimens. Among the reasons for the failure of the calculation, one of the main ones consists apparently in the incorrect initial assignment of certain frequencies. The selection of the force field, in which certain important interactions, for example, those of the N(5)–C(4*a*) and C(10*a*)–N(1) bonds, were altogether disregarded, was also relatively unsuccessful (Fig.3). We may note that the initial approximation chosen by the authors proved to be relatively unsuitable also for uracil, where the calculation likewise reproduced unsatisfactorily the increase of the frequencies in the region of 1250 cm^{-1} on deuteriation.[69] Thus only preliminary conclusions may be made so far concerning the nature of the individual resonance Raman bands of flavins, mainly on the basis of isotope substitution data.[61,64,67]

Band I. The highest-frequency 1630 cm^{-1} band has been assigned in most investigations to vibrations with the predominant involvement of the benzene ring, mainly on the basis of the appreciable decrease of this frequency following substitution by halogen atoms in the 7- and 8-positions.[61,70] This Raman line proved to be almost insensitive to isotope substitution in the 2-, 4*a*-, 5, 1, and 3-positions;[67] it hardly shifts for the 1,3- and 5-deaza-derivatives[71] and is not intensified on resonance excitation at the frequency corresponding to the long-wavelength (α) absorption band. All the data obtained hitherto show that the symmetrical (ν_s) and anti-symmetrical (ν_{as}) vibrations of the C(2)=O and C(4)=O carbonyl groups are not manifested in the resonance Raman spectrum.

Band II (1548 cm^{-1}). This band changes appreciably on substitution of the N(5), C(4*a*), and C(10*a*) atoms in ring II[67] and disappears in 5-deaza-FMN.[71] However, the appreciable involvement of other coordinates is indicated by the shift of this band in the *N*(3)-substituted derivatives.[71] On resonance excitation at the frequency of the β-band (370 nm), it was possible to observe only this line.[62]

Table 2. The shifts of the resonance Raman lines of the N(3)H forms of the isotope-substituted riboflavin specimens.[67]

ν, cm^{-1}[a]	^{13}C			^{15}N		
	2-	4*a*-	2.4.4*a*,10*a*-	5-	1.3-	1,3.5-
1631 (1630)	2	1	2	1	1	2
1584 (1582)	3	8	13	4	1	5
1548 (1548)	6	5	21	3	2	4
1503 (1409)	3	2	7	1	2	4
1465 (1462)	5	6	8	1	3	6
1407 (1406)	3	5	12	1	4	6
1355 (1351)	4	3	15	0	1	1
1302 —	0	2	5	0	0	2
1282 —	0	2		0	0	0
1252 (1295)	14	0	17	0	10	10
1229 (1232)	0	3	4	0	2	2
1179 (1181)	3	4	8	2	4	6
1161 (1147) (1138)	1	2	5	1	1	2
1073 —	3	3	3	—1	4	2
994 (990)	2	0	4	0	1	3
834 (832)	2	0	2	5	5	10
789 (772)	2	0	4	2	2	6
740 (744)	1	0	2	1	0	2
633 (629)	1	—1	0	—1	1	2
605 (602)	4	1	4	1	1	4
576 —	3	4	5	9	2	9
521 (522)	1	1	2	4	1	7
496 (474)	1	2	—	1	2	4
429 (427)	2	2	2	3	0	6

[a] The frequencies for the N(3)D form are given in brackets.

Band III. Large isotope shifts (21 cm^{-1} in the 2,4,4*a*,10*a*-^{13}C-substituted derivatives (Table 2) have been observed for the low-intensity 1548 cm^{-1} line.

Bands IV, V, and VI. The weak bands at 1500 cm^{-1} (IV) and 1462 cm^{-1} (V) and the intense 1407 cm^{-1} band (VI) are approximately equally sensitive to isotope substitution. The 1407 cm^{-1} vibration is appreciably delocalised; the shifts of this band are large on ^{13}C and ^{15}N isotope substitution in ring (III) and amount to approximately 10 cm^{-1} in the 7,8-dichloro-derivatives.[61]

Band VII. The 1355 cm^{-1} band is one of the most intense in the resonance Raman spectrum. It has been noted that it is intensified on resonance with the electronic absorption α-band (450 nm) and is the most intense on excitation in the pre-resonance region.[63] Table 2 shows that the corresponding vibration is very sensitive to ^{13}C substitution and is relatively insensitive to ^{15}N substitution. However, this finding is not in any "conflict" with the decrease of the frequency of this line in the deaza-derivatives,[71] since a different system of conjugated bonds is formed on replacement of the N(1) and N(5) atoms by carbon atoms.

Bands VIII and IX. The very weak lines at 1302 cm^{-1} (VIII) and 1282 cm^{-1} (IX) are almost insensitive to isotope substitution.

Bands X, XI, XII, and XIII (1255, 1228, 1182, and 1160 cm^{-1}). The greatest changes occur in this group of bands on replacement of the N(3)H proton by deuterium and were noted in the very early studies;[58] not only the line frequencies but also the relative line intensities change significantly under these conditions (Fig.6). Evidently the $\nu = 1295$ cm^{-1} band is the analogue of the intense 1255 cm^{-1} band in the spectrum of the deuteriated specimen. The increase of the frequency by more than 40 cm^{-1} is usually explained, after Kitagawa,[61] by the breakdown of the "resonance" interaction of the C–N stretching vibration (tentatively at 1290 cm^{-1}) with the in-plane NH deformation vibration, which reduces this frequency in the non-deuteriated specimen.§ However, we may note that the idea of "resonance" in interactions of the vibrations is altogether unnecessary for the explanation of the observed changes. Evidently, the frequency considered can increase even as a result of a slight involvement of the fairly rigid N–D bond when the amplitude of the stretching vibration of the deuterium atom is large. If this hypothesis is correct, then the replacement of the N(3)H hydrogen by the methyl-group should entail an increase in frequency, which has been observed experimentally for *N*(3)-methyl-lumiflavin.[70] It is evident from these ideas that the change in the 1255 cm^{-1} frequency can serve as a criterion of the strength of the hydrogen bonding of the N(3)H group of flavin with the solvent or the aminoacid residues in the active centre of the protein; the frequency should increase as a result of the increase of the effective rigidity of the C–N(3)–H angle as a consequence of the additional binding of the hydrogen atom (see below).

Among the remaining bands of this group, the 1179 cm^{-1} band partly corresponds to the most "delocalised" vibration. The 1179/1160 cm^{-1} band pair undergoes an appreciable change in the relative intensities on isotope substitution[67] also in *N*(3)-derivatives[61] and also on substitution by heavy atoms in the 7- and 8-positions.[61] Evidently any kind of reliable assignments in this region are impossible without a reliable calculation of the normal vibration frequencies; there appears to be little justification for the scheme of frequency shifts on deuteriation proposed by Schmidt et al.[64] (with the exception of the 1255 → 1290 cm^{-1} shift discussed above). Data for the region below 1100 cm^{-1} have also been obtained;[67] the greatest isotope shifts are apparently localised in ring II and have been observed for the 834 cm^{-1} band, while the greatest shifts on deuteriation are those of the 789 and 496 cm^{-1} frequencies.

The Hydrogen Bonds Involving the Isoalloxazine Ring in the Active Centres. Since the prosthetic flavin group does not in most cases form a covalent bond with apoprotein, hydrogen bonding is important for the stabilisation of the structure. The change in the distribution of electron density in the isoalloxazine ring on formation of hydrogen bonds is evident from the changes in the electronic absorption spectra in model systems (see Yagi and co-workers[73,74] and the references in the latter communication). As already mentioned, the frequencies and intensities of the bands in the range 1160–1300 cm^{-1} are sensitive to hydrogen bonds in the resonance Raman spectra. The hydrogen bonding of flavins has been studied experimentally by Schmidt et al.,[64] who compared the spectra of model flavins in H_2O (a powerful hydrogen bond donor and acceptor), dimethyl sulphoxide (DMSO) (a polar solvent which is a weaker acceptor than H_2O), and acetonitrile (a polar solvent). Potassium iodide was added to suppress fluorescence. On passing from aqueous solutions to DMSO, a change in the relative intensities of bands II and X and a decrease of the frequency of band X were noted. In the subsequent discussion the weak 1281 cm^{-1} band was used as an "indicator" of hydrogen bonding; however, it has been shown[67] that the corresponding vibration is insensitive to any kind of isotope substitution in rings III and II, i.e. at the sites where the hydrogen bonds are localised.

On the basis of these model studies, the authors attempted to examine the hydrogen bonds in the active centres of three FAD-containing flavoproteins of different classes and reached the following conclusions: (1) the acyl-CoA-dependent general aliphatic acid dehydrogenase is characterised by a "somewhat reduced" hydrogen bonding compared with FAD in H_2O; (2) acyl-CoA-oxidase does not form at all or forms only weak hydrogen bonds in all the potential N(1), N(5), C(2)=O, C(4)=O, and N(3) hydrogen bonding centres; (3) glutathione reductase is bound to the same extent as the free FAD group in water.

However, examination of the data of Schmidt et al.[64] (Fig.8) shows that the real situation is much more complex than the above simplified picture. In the case of acyl-CoA-dehydrogenase, the 1253 cm^{-1} band has an unusually high intensity, which may be a result of strong hydrogen bonding. X-Ray diffraction data have not as yet been obtained for acyl-CoA-oxidase, but the paradoxical conclusion that there is no hydrogen bonding in flavins of this class conflicts both with the entire experience gained in the steric studies on flavoproteins[34] and with the UV spectroscopic data.[74] An attempt has been made[74] to estimate the influence of hydrogen bonding on the electronic transition energies and absorption band intensities by modelling the hydrogen bond involving the heteroatom in the isoalloxazine ring (O or N) in the MO SCF calculation by variations in the ionisation potential of the valence state. The authors carried out calculations in this way for all the possible variants of hydrogen bonding; in the light of these results, the experimental electronic spectroscopic data for oxidases should correspond to a strong hydrogen bond at N(5).[74] The resonance Raman spectrum of glutathione reductase in the region 1300–1200 cm^{-1} has a complex contour made up of four incompletely resolved bands,[64] which differs completely from the picture for free FAD in aqueous solution. The resonance Raman

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§ As already mentioned, this shift has an analogy with that observed in the Raman spectrum of uracil;[72] however, the increase of the frequency in the latter on deuteriation is only by 16 cm^{-1}.

spectroscopic data refer to glutathione reductase from yeast; the three-dimensional structure of the glutathione reductase from erythrocytes has been determined recently with a high resolution;[36,37] in this complex protein the isoalloxazine ring brings the subunits into contact by means of hydrogen bonding between the N(3)H proton of the FAD in one subunit and the histidine residue in the main chain of another subunit; the N(1) and N(5) atoms form strong hydrogen bonds with the aminoacid residues of the active centre. Since glutathione reductase contains two FAD domains, it is quite possible that the complex contour of the resonance Raman spectrum can be accounted for by certain differences in the orientation and strength of the hydrogen bonds of the two isoalloxazine rings.

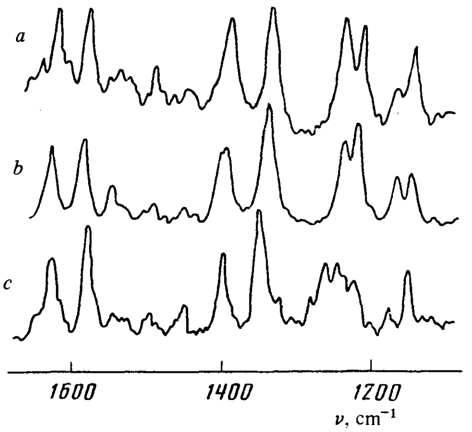

Figure 8. The resonance Raman spectra of aqueous solutions of certain flavoproteins:[64] *a*) acyl-CoA-dependent general aliphatic acid dehydrogenase (pH 8.4; λ = 488 nm); *b*) aliphatic acid acyl-CoA-oxidase (pH 8.0; λ = 488.0 nm); *c*) yeast glutathione reductase (pH 7.6; λ = 514.5 nm).

Flavodoxins. Flavodoxins are the smallest of the FMN-containing proteins; both long (~170 aminoacid residues)[75] and "short" (138 [35] and 148 [76] residues) flavodoxins fulfil identical biological functions; they transport one electron to other flavin systems, proteins with Fe/S centres, or haemoproteins. The two one-electron oxidation-reduction potentials of these molecules differ significantly, which makes it possible to characterise three forms; the oxidised form, the semiquinone (radical), and a reduced form, which makes the flavodoxins convenient model compounds. The resonance CALS spectra with excitation frequency of the long-wavelength absorption band have been obtained[66,78] for representatives of two classes of flavodoxins isolated from the bacteria *Clostridium* and *Desulfovibrio*, which differ in the aminoacid sequences, electronic spectra, and ability to bind riboflavin.[77]

High-resolution X-ray diffraction data are available for the same proteins,[35,76,79] which permits a comparison with the possible interactions with the resonance Raman spectroscopic parameters. It has been shown for flavodoxins of both types that the ribityl component "immersed" in the protein environment forms strong hydrogen bonds with the latter. The planar isoalloxazine ring is disposed nearer to the surface of the globule, but its contacts with the solvent or with an electron donor are strictly limited by the protein environment, which "closes" the pyrimidine and central pyrazine windows, so that only the dimethylbenzene component is accessible to external contacts. Fig. 9 illustrates the system of hydrogen bonds postulated for FMN in the active centre of the *Desulfovibrio vulgaris* flavodoxin.[76] Evidently, with the exception of N(1), all the donor and acceptor atoms are hydrogen-bonded, i.e. the situation in this instance is analogous to FMN in an aqueous environment. Nevertheless, on comparing the CALS spectrum (Table 3) of this flavodoxin with the spectrum of FMN in H_2O, the authors[66] noted a change in frequencies (cm^{-1}): 1629 (free)–1624 (bound); 1582–1573; 1412–1407; 1261–1251; 1233–1227; 1192–1185. The intensity of certain bands changes even more appreciably than the frequency, which is particularly notable in the region 1100–1300 cm^{-1}. As already mentioned, the low frequency (1251 cm^{-1}) and the low intensity of this line

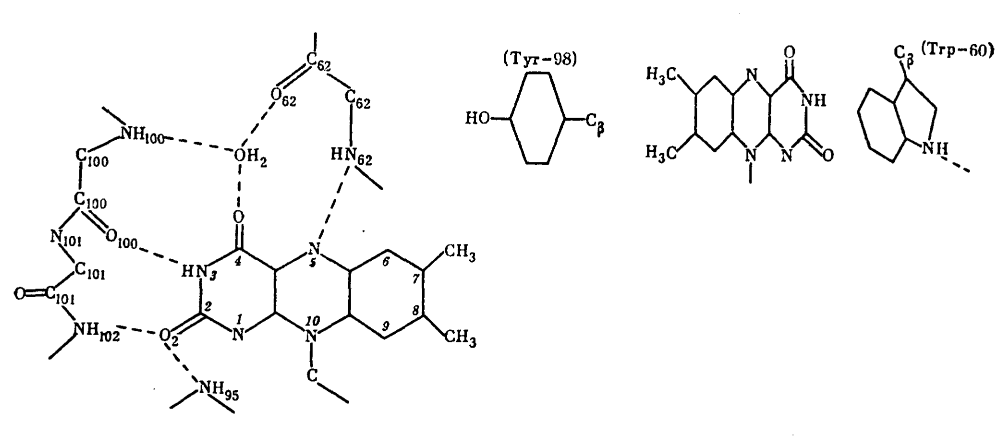

Figure 9. A tentative system of hydrogen bonds of the isoalloxazine ring in the active centre of the flavodoxin of *Desulfovibrio vulgaris*;[76] the numerals represent the numbering of the aminoacid residues in the protein chains; slight rotation of the residue 62 permits the formation of a hydrogen bond with the N(5) atom; the orientation of the flavin relative to the tryptophan and tyrosine residues is shown above.

most probably indicate a decrease of hydrogen bonding along the section C(2)O–N(3)–C(4)O. Among the remaining differences, the decrease of the frequency and intensity of the 1571 cm^{-1} band are the most significant; bearing in mind the sensitivity of the corresponding vibration to isotope substitution,[67] one can postulate a change in electron density in ring II as a result of the binding of N(5). However, there is also another possibility; the isoalloxazine ring in the active centre of flavodoxin is sterically close to the indole ring of the tryptophan-60 residue and the aromatic ring of tyrosine-98 (Fig.9). It is known that the intense fluorescence of the FMN in flavodoxins is entirely quenched; a stacking interaction of the isoalloxazine ring with tryptophan has been suggested as the quenching mechanism.[79] One cannot rule out the possibility that the change in the intensity of the 1573 cm^{-1} band is associated with an interaction of this type. However, we may note that the flavin and indole rings are in this case non-coplanar and make an angle of 45°, which renders the charge-transfer interaction problematical.

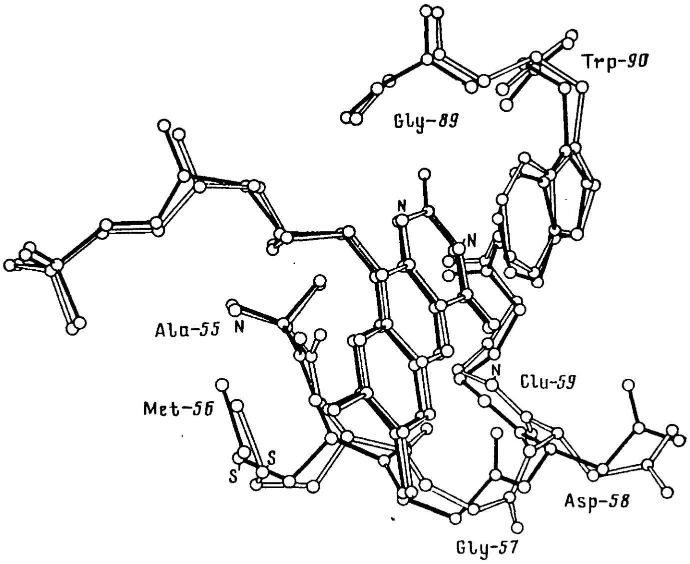

Figure 10. The orientation of the aminoacid residues 55–59 and 89–90 relative to the isoalloxazine ring in the active centre of the oxidised (light lines) and semiquinone (dark lines) form of the flavodoxin of *Clostridium MP.*[35]

Another flavodoxin from a *Desulfovibrio* of the same class (*Desulfovibrio gigas*), whose three-dimensional structure is unknown, has also been investigated by resonance Raman spectroscopy.[66] While the aminoacid compositions of the *gigas* and *vulgaris* flavodoxins are similar, their abilities to bind FMN were found to be different.[75] The CALS spectra demonstrate unambiguously that the immediate environment of the FMN in the active centres of the two proteins considered should be completely identical.[66]

A representative of another class of flavodoxins (from *Clostridium*), fulfilling analogous biological functions, differs significantly in many details of the environment of the isoalloxazine ring, whilst there is an overall homology of the three-dimensional structure with those of the proteins of the *Desulfovibrio* type examined above and the binding of the ribityl phosphate component is very similar.[35,79] However, despite the differences in the chemical sequences, in the active centres of proteins of these classes there is a considerable analogy of the steric structures, which apparently in fact plays a decisive role in their functioning. In the *Clostridium* flavodoxin the pyrimidine and pyrazine rings are likewise "close", the typtophan-90 residue is close to the pyrimidine component (at an angle of 27°), and the orientation of the Gly-57 residue, the interaction with which is tentatively believed to stabilise the semiquinone form (see below), is equivalent to the orientation of Gly-61 in the *Desulfovibrio* flavodoxin.[76] The CALS spectrum of the *Clostridium* flavodoxin[78] is in general similar to the spectra of the *Desulfovibrio* proteins obtained under the same excitation conditions (ω_1 = 480 nm[66]); a decrease of the frequency and intensity of the 1577 cm^{-1} line (tentatively assigned to the flavin–tryptophan interaction) is observed in this case also, but the changes in the relative intensities of the bands in the range 1100–1300 cm^{-1} indicate a different character of the hydrogen bonding in the active centre of the *Clostridium* flavodoxin. The high quality of the CALS spectrum,[78] for which the authors were able to obtain reliable data in the region below 1000 cm^{-1}, is noteworthy. The character of the low-frequency section of the spectrum proved to be significantly different than for free FMN.[63] There is no doubt that analysis of the low frequencies made it possible to obtain subsequently additional information about the electronic rearrangements and interactions of the prosthetic flavin group in the active centres of the proteins.

Table 3. The frequencies (cm^{-1}) in the resonance Raman spectra of certain flavoproteins.

Band designation	RBP (Ref.67)[a]	Flavodoxins			GO (Ref.58)[e]	CoA (Ref.164)[f]	CoA (Ref.64)[g]	GR (Ref.64)[h]
		gigas (Ref.66)[b]	*vulgaris* (Ref.66)[c]	Cl.MP (Ref.78)[d]				
I	1631	1624	1626	1628	1626	1624	1698	1627
II	1584	1573	1571	1577	1578	1583	1586	1580
III	1548	1545	—	—	—	1544	1551	—
IV	1503	1501	1501	1505	1501	1496	1498	—
V	1465	—	—	—	—	1454	1460	—
VI	1407	1407	1407	1409	1404	1407	1412 1403	1402
VII	1355	1352	1354	1356	1364,1345	1352	1351	1353
VIII	1302	—	—	—		—	—	1281
IX	1282	—	—	1279	—	—	—	1261
X	1252	1251	1254	1257	—	1253	1251	1246
XI	1229	1227	1223	1231	1230	1231	1233	1224
XII	1179	1173	1185	1179	1182	1182	1182	1180
XIII	1161	1163	1164	1165	1158	1162	1162	1155

[a] RBP = riboflavin-binding protein from chicken egg protein, pH 7, λ = 488.0 nm. [b,c] CALS, ω_1 = 480 nm. [d] Clostridium MP, pH 7.3, CALS, ω_1 = 480 nm. [e] Glucose oxidase, CALS, ω_1 = 480 nm. [f] Acyl-CoA-dependent aliphatic acid dehydrogenase; here and henceforth there was spontaneous RS with λ = 488.0 nm at pH 8.4. [g] Acyl-CoA-oxidase (from yeast), pH 8, λ = 488.0 nm. [h] Glutathione reductase (from yeast), pH 7.6, λ = 514.5 nm.

The Semiquinone Form. A key property of flavoproteins, as one-electron transferring agents, is the thermodynamic stabilisation¶ of the intermediate radical state—the so-called

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¶ See, for example, the references in the paper of Smith et al.[35] concerning the association of the semiquinone form with the particular protein compared with the oxidised form on energy grounds.

semiquinone form (Fig.3). The electronic absorption spectra of model systems and flavoproteins with a stabilised semiquinone form contain intense bands due to the $\pi \rightarrow \pi^*$ transitions in the range 500–600 nm (Fig.5),[55] which indicates the retention by the isoalloxazine ring of the planar structure characteristic of the oxidised form; this is also demonstrated by the electronic nuclear double resonance (ENDOR) spectra.[80] These conclusions have been fully confirmed by X-ray diffraction data.[35]† It follows from Fig.10, where the disposition of the aminoacid residues closest to the flavin in the active centre is illustrated for the oxidised and semiquinone states of the flavodoxin, that the formation of the semiquinone form is unaccompanied by any radical changes in the orientation of the isoalloxazine ring in the active centre. At the same time the conformational rearrangements of certain aminoacid residues, particularly along the Gly-57–Asp-58 section, are apparently decisive for the stabilisation of the semiquinone. A special role has been attributed[35] to the change in the orientation of the Gly-57 residue by approximately 180°; as a result, conditions are created in the semiquinone for the formation of the N(5)...O (Gly-57) hydrogen bond and the dissociation of the O(4)...NH (Asp-58) hydrogen bond, which may exist in the oxidised form. According to Smith et al.,[35] the N(5)...O (Gly-57) binding is a decisive stabilising factor;# the shift of the atoms of the other residues in the active centre (with the exception of Asp-58) is on average 0.5 Å; the orientation of the tryptophan residue relative to the plane of the isoalloxazine ring also changes somewhat. We may note that these conformational rearrangements fully correspond to 3.4 kcal mol^{-1}—the preferential energy of the association of the semiquinone form relative to the oxidised form. A study[55] of the polarisation absorption spectra of flavodoxin crystals showed that the electronic α- and β-transitions in the oxidised and semiquinone forms (in terms of the author's notation[55]) are linearly polarised in the plane of the flavin ring with the direction of the transition moment closer to the N(5)–N(10) axis (Fig.6) for both the α- and β-bands. The most interesting conclusion reached by the above investigators[55] is that, in the electronic spectra of the semiquinone structure, both low-energy $\pi \rightarrow \pi^*$ transitions take place between orbitals of the same type as in oxidised FMN. This hypothesis is apparently confirmed by the following experimental observations:[55] (1) similar band polarisation ratios; (2) similar β-band contours and similar frequencies observed in the diffuse vibrational structure of the α-band (the 0–0 and 0–1 transitions respectively at 21000 and 22000 cm^{-1}) for the oxidised form and at 1620 and approximately 17300 cm^{-1} for the semiquinone form; (3) similar correspondingly normalised intensities. The identical signs for the α- and β-bands observed in the circular dichroism spectra of both forms and the similar anisotropies of the transitions may also serve to support the above hypothesis.[81] Thus if the hypothesis is valid, the formation of the semiquinone structure should be represented by the addition of one electron to the unoccupied π orbital of the oxidised form without a significant redistribution of electron density.

Apart from the information about the change in electron density in the semiquinone, the identification of this structure on the basis of Raman spectroscopic data may prove to be especially useful also because the manifestations of the semiquinone form in the electronic spectra of flavoproteins are frequently similar to those observed on formation of charge-transfer complexes (see, for example, Massey and Hemmerich[43] and the references quoted therein). The resonance Raman spectra have now been obtained for the semiquinone forms of two proteins, namely flavodoxin[78] and the riboflavin-binding protein,[82] and also for the semiquinone forms of FMN and FAD stabilised by the methylation of the N(5) atom.[83] As might have been supposed, the change in bond orders in ring II led to changes in almost all the vibration frequencies of the flavin system (Table 4). On excitation in the region of the β-transition of the semiquinone (λ = 514.5 nm; Fig.11), the 1611 cm^{-1} band predominates in the spectrum;[83] as the α-transition is approached, its intensity diminishes[82] and, after excitation at the frequency corresponding to the long-wavelength slope of the absorption α-band, the band at approximately 1340–1370 cm^{-1} becomes most intense.[83] It has been suggested[78,83] that the intense 1611 cm^{-1} line of the semiquinone is an analogue of the 1580 cm^{-1} line of the oxidised form and that the corresponding vibration is localised mainly in ring II. However, bearing in mind the reduced bond orders in ring II and also the displacement of the unshared electron pair of the N(5) atom from the conjugation system on formation of the semiquinone structure, a decrease (and a fairly large one) of the corresponding frequency might

Table 4. The frequencies of the resonance Raman lines of the semiquinone structures of flavins^{a}.

Flavin	ν, cm^{-1}												Refs.
RBP^{b} (H_2O)	1617 s	1582 w	1553 w	—	1407 w	1393 сл	1350 m	—	1273 w	1230 m	1160 v.w	1082 w	
" (D_2O)	1618	1585	1535		1407	1387	1353					1089, 1060	[82]
Flavodoxin^{c} (H_2O)	1611 s	—	—	—	—	1391 s	1378 m	1333 w	1269 m	1232 s	—	—	[78]
" (D_2O)	1611					1386							
5-Me-FAD^{d}	1611 v.s	1590 m	—	1476 w	—	1372 w	1351 m	1330 m	1278 w	1224 w	—	—	
" ^{e}	1611 m	1590 m	1516 m	1432 m		1372 v.s	—	1330 v.s	1278 w	1224 m	1174 m		[83]
5-Me-FMN^{f} (H_2O)	1613 m	1590 m	1516 w	1443 v.w	—	1376 v.s	—	1334 v.s	1282 v.w	1224 m	1179 m	—	
" (D_2O)	1611 m	1588 m	1514 w	1446 w		1372 v.s		1334 v.s	1256 v.w	1204 w	1178 m		[83]
8-Cl-5-Me-FMN^{f}	1613 w	1590 m	1516 w	1443 w	—	1378 v.s	—	1334 s	—	1226 w	1170 m	—	[83]

^{a}For the region above 1000 cm^{-1}. $^{b}\lambda$ = 514.5 nm. ^{c}CALS, ω_1 = 620 nm. $^{d}\lambda$ = 514.5 nm. $^{e}\lambda$ = 647.1 nm. $^{f}\lambda$ = 641.7 nm.

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†The "folding" angle relative to the N(5)–N(10) axis (Fig.5) is 2.5° in the semiquinone.[35]

#In the flavodoxins of the *Desulfovibrio class*,[76] this role is fulfilled by the Gly-61 residue; the H(62)–O(4) bond is possible in the oxidised form of the protein.

have been expected. Furthermore, the 1611 cm^{-1} line is almost insensitive to either methylation of the N(5) atom[83] or to the deuteriation of the semiquinone structures in which an exchangeable proton is present at the N(5) atom.[78,82] Thus the resonance Raman spectra can be used as a reliable criterion in the identification of the semiquinone structure, which has in fact been done[84] in studies on the NADP complex with adrenodoxin reductase. However, the Raman resonance spectroscopic data obtained hitherto cannot be used to either confirm[78,83] or reject Eaton's hypothesis.[55] In order to solve this problem, detailed studies of the dependence of the resonance Raman lines on the exciting frequency (the excitation spectra) in the region of the α- and β-electronic transitions of the semiquinone are necessary. On the other hand, the proposed correlations of the resonance Raman frequencies of the semiquinone and oxidised structures[83] can be reliably established only on the basis of data for isotope-substituted specimens.

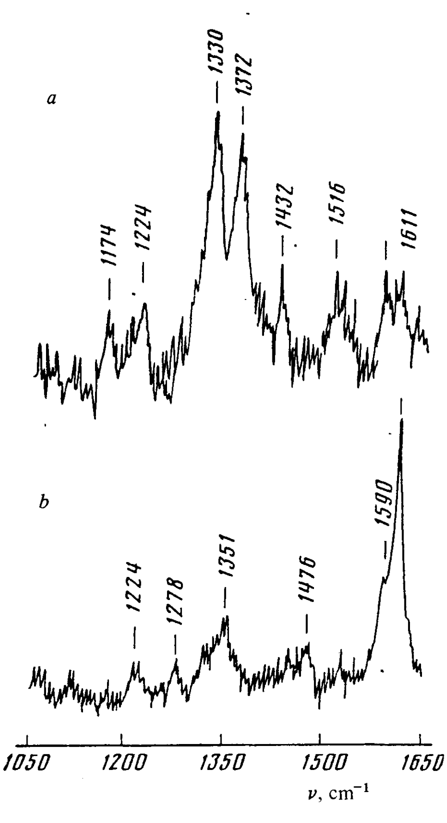

Figure 11. The spectra of *N*(5)-methyl-FAD in the semiquinone form; spontaneous RRS; excitation wavelengths (nm): *a*) 647.1; *b*) 514.5.[83]

Reduced Flavins. The fully reduced isoalloxazine ring undergoes electronic transitions at shorter wavelengths than the oxidised and semiquinone forms (Fig.12), a factor making difficulties in the measurement of the resonance Raman spectra. The latter have been obtained comparatively recently only for structures where the reduced form gives rise to a charge-transfer complex. The so-called "purple complexes", formed at the intermediate stages of the reaction of D-aminoacid oxidase (DAO) with D-alanine and D-proline, have been investigated.[85-88] These complexes have a characteristic long-wavelength absorption extending to approximately 750 nm. On excitation with light at wavelengths in the region of the long-wavelength band, a resonance intensification of the lines of both the substrate (alanine and proline) and of the active centre of the enzyme (FAD) was observed. Using numerous verions of isotope substitution in the isoalloxazine ring and in the substrate molecules, the authors[85-88] assigned the frequencies with exceptional reliability and demonstrated that, (1) the isoalloxazine ring in the purple complex exists in the fully reduced form, (2) the ~1605 cm^{-1} vibration of the flavin, which intensifies more than others on excitation at wavelengths corresponding to the charge-transfer band, is localised in the C(10*a*)–C(4*a*)–C(4) = 0 fragment, and (3) the 1692 cm^{-1} band in the complex with D-alanine and the 1658 cm^{-1} band in the complex with D-proline refer to the C=N§ stretching vibrations of aminoacids, which are thus involved in the imino-form in the complex formation reaction. An interesting and hitherto unexplained feature of the complexes with D-alanine is the sensitivity of the ~1540 cm^{-1} line to isotopic substitution in both the substrate molecule and in FAD.[88]

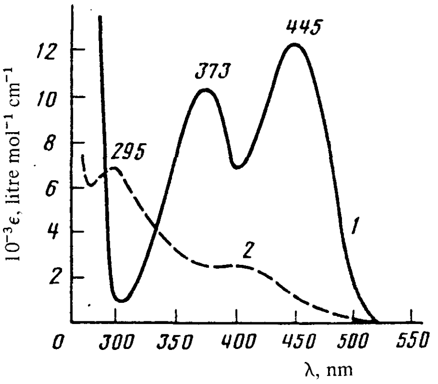

Figure 12. The electronic absorption spectra of the fully oxidised (curve *1*) and fully reduced (curve *2*) forms of FMN.[43]

The resonance Raman data obtained provide direct evidence that the C(10*a*)–C(4*a*)–C(4)=O fragment of reduced FAD in the purple complex is in close contact with the HN = C–COO⁻ plane of the substrate, ensuring an interaction of the charge-transfer type.

Charge-Transfer Complexes. One of the most important features which is apparently essential for the functioning of many flavin systems is their ability to form charge-transfer complexes (CTC); such complexes are formed by almost all flavoenzymes containing pyridine nucleotide.[89] Data obtained recently on the three-dimensional structure of glutathione reductase[36,37] confirmed that the NADP ring in the active centre is indeed located above the isoalloxazine ring in a conformation favourable for the formation of a

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§ The changes in these frequencies in the deuteriated specimens indicate an appreciable involvement of δ(NH) in the vibration.

charge-transfer complex. Certain flavo-proteins are known to be capable of undergoing charge-transfer interactions also with other substrates, in particular with benzene derivatives.[89] The mechanisms of the formation of such complexes, their structure, and their catalytic value are still in many respects obscure. The formation of CTC of flavins is usually inferred from the appearance of a long-wavelength absorption in the range 500–700 nm, which is accompanied as a rule by a decrease of the intensity of the α- and β-bands, but these changes, as already stated, are extremely similar to those observed for semiquinone flavin structures. Resonance Raman spectroscopic data have been obtained recently for a series of model CTC of flavoproteins: it is now already evident that the resonance Raman spectra make it possible to identify reliably the CTC of flavins and can yield, in principle, unique information about the structure and about the site of the charge transfer.

The first model for the study of the CTC of flavins was the so-called old yellow enzyme (OYE) containing the FMN prosthetic group. In nature, this protein exists in the "green" form—a complex with *p*-hydroxybenzaldehyde;[90] it is also capable of forming artificial complexes with a wide variety of aromatic and heteroaromatic derivatives containing hydroxy-groups.[43,90] Japanese workers[91,92] investigated the resonance Raman spectra of the products of the interaction of OYE with a set of substituted phenols on excitation at the wavelength corresponding to the long-wavelength absorption band. Analysis of the data obtained shows in the first place that, in the complexes investigated, the flavin is present in the oxidised state; the 1628, 1585, 1548, 1415, 1356, 1260, and 1160 cm^{-1} bands present in the spectra of all the specimens have virtually the same frequencies as in the spectra of FMN and riboflavin. At the same time a resonance intensification of the bands (especially in the low-frequency section), specific to the substituted substrate, is observed in the resonance Raman spectra at 477, 390, 475, 386, and 547 cm^{-1} respectively for *p*-CH_3, *p*-Cl, *p*-F, *p*-NO_2, and other substituted phenols respectively. In the high-frequency region, it is also possible to identify bands referring to the phenolic component, which is especially apparent for complexes with pentachloro- and pentafluorophenols.[92] Studies on the frequency dependence of certain resonance Raman lines in the charge-transfer band[92] have shown that the 1588 cm^{-1} frequency of isoalloxazine and the 1475 and 454 cm^{-1} frequencies of phenol make the greatest contribution to the vibrational structure of the long-wavelength electronic absorption band (Fig.13).

In this case the spectra do not exhibit frequencies referring directly to the C–OH fragment of phenol, which is characteristic of, for example, the complexes of the phenoxide anion with metals, but the interaction takes place locally via the phenolic oxygen atom. The character of the dependence of the intensity on the excitation frequency $I(\nu)$ for the 1588 cm^{-1} line[92] yields direct evidence for charge transfer to the flavin ring. Since the corresponding vibration is associated predominantly with the N(5)–C(4*a*)–C(10*a*) fragment, these data make it possible to infer the location of the charge transfer. The occurrence of such interaction requires a sandwich conformation with parallel isoalloxazine and phenol rings. The constancy of the frequency of the 1588 cm^{-1} band (as for the remaining frequencies of the isoalloxazine ring) shows that all the changes in electron density refer exclusively to the excited state of the molecules. The greatest charge transfer occurs in the complex with *p*-nitrophenol, which can be inferred from the change in the distribution of intensities in the resonance Raman spectrum.

The same characteristic features have been noted in the resonance Raman spectra of the charge-transfer complexes of other flavoenzymes obtained at present. In the study of the complexes of the CoA-dependent aliphatic acid dehydrogenase (containing FAD) with acetoacetyl-coenzyme A, the authors observed a resonance intensification of the 1586 and 1550 cm^{-1} lines,[94] confirming thereby the fact that the electron transfer in the interaction with the most varied donors is directed to the N(5) and C(4*a*) centres of the isoalloxazine ring, in agreement with quantum-chemical calculations.[95] Artificial complexes of D-aminoacid oxidase with amino- and hydroxy-benzoates have also been studied:[96] the latter are known to be effective inhibitors of the enzyme. On excitation at the frequency corresponding to the long-wavelength absorption band (λ = 632.8 nm) of the complex of DAO with *o*-aminobenzoate, the 1583 cm^{-1} (isoalloxazine ring) and 568 cm^{-1} (*o*-aminobenzoate) lines were observed. It is of interest that resonance intensification has not been observed for the *meta*- and *para*-aminobenzoates, which indicates severe conformational limitations in the formation of the CTC.

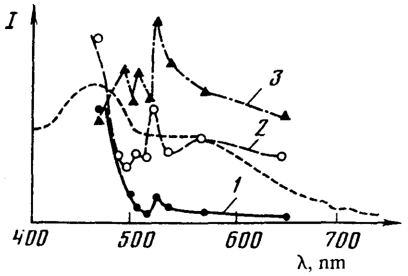

Figure 13. Dependence of the intensity of certain spontaneous resonance Raman lines of the complex of old yellow enzyme with pentachlorophenol on the frequency of the exciting light; the intensification of the lines of the flavin component [*1*) 1628 cm^{-1}; *2*) 1588 cm^{-1}] and the ligand [*3*) 1475 cm^{-1}] can be seen; the contour of the absorption band is shown by a dashed line.[92]

In the reaction of pig liver DAO with β-cyano-D-alanine, the intermediate stages also consist of CTC of the oxidised flavin according to resonance Raman spectroscopic data.[97] We may note that, in the spectra of all the DAO complexes investigated, the "hydrogen bond indicator" band is at 1240 cm^{-1},¶ [96,97] i.e. is appreciably displaced towards lower frequencies compared with other flavins, which indicates extremely specific interactions of FAD with the DAO apoprotein. Charge-transfer complexes have been identified also in the intermediate stages of the anaerobic reduction of adrenodoxin reductase by the NADP coenzyme.[98]

Metal Complexes. The problem of the interaction of flavins with metals is important for the understanding of the mechanisms of the functioning of flavoproteins containing Fe/S centres and also molybdenum.[99] The model complexes of FMN with silver and ruthenium[100] and the complexes of the riboflavin-binding protein (RBP) and 10-methylisoalloxazine with ruthenium(II) have been investigated.[100,101] The electronic absorption spectra of the silver(I) complex of FMN contain a weak shoulder at approximately 530 nm on the

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¶ The assignment of this band in the spectra of the DAO complexes has been confirmed by the 1242 → 1284 cm^{-1} shift on deuteriation.

long-wavelength slope of the α-band, while an intense band at ~630 nm appears in the spectra of the complexes $(NH_3)_4Ru^{II}$ (Fig.14).

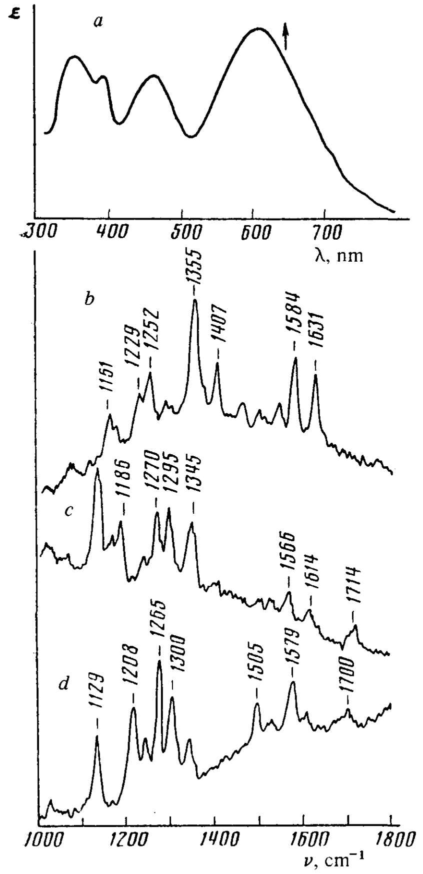
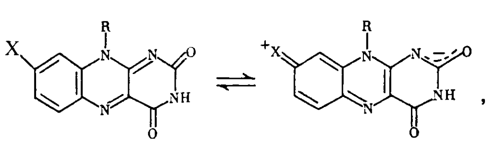


Figure 14. The electronic absorption spectrum of the complex of the riboflavin-binding protein with $Ru^{II}(NH_3)_4$ (*a*) and the spontaneous resonance Raman spectra: *c*) the RBP–$Ru^{II}(NH_3)_4$ complex; *d*) the complex of $Ru^{II}(NH_3)_4$ with 10-methylisoalloxazine; excitation at $\lambda = 647$ nm (indicated by an arrow on the absorption spectrum) was used in both cases; *b*) the spectrum of RBP ($\lambda = 488.0$ nm) is presented for comparison.[101]

The resonance Raman spectroscopic data may permit the conclusion that the interaction in the Ag^+ FMN complex is of the charge transfer type. Apart from the N(5) atom (whose involvement can be inferred from the increase of the intensity of the 1580 and 1540 cm^{-1} lines), the oxygen atom closest to N(5) apparently also participates in the reduction; this is indicated by the changes in the symmetric and antisymmetric vibrations of the carbonyl groups in the infrared spectrum of the complex Ag^+ FMN.[100] On formation of the complex of $Ru^{II}(NH_3)_4$ with RBP,[101] the frequencies and relative intensities of almost all the lines in the resonance Raman spectrum are altered. The frequencies and particularly the distribution of the intensities on excitation at 647.1 nm (Fig.14) resemble most closely those observed for the semiquinone form (Section 5). However, this hypothesis requires further tests. It is of interest that bands at ~1700–1710 cm^{-1}, referring to the carbonyl groups, are manifested in the resonance Raman spectrum of Ru^{II}RBP as well as in the spectrum of the model ruthenium(II) complex of 10-methylisoalloxazine.[101]

The data obtained for the model metal complexes established[102] that there is no direct electron transfer between the Fe/S cluster and the flavin in the ETF hydrogenase,† an FAD-containing flavoprotein, which incorporates Fe/S centres and functions in the electron transport chain, although such transfer might have been postulated on the basis of the EPR spectra (see the references in the paper of Schmidt et al.[102]).

Modified Flavins. As already mentioned, in many cases the prosthetic group of the flavin can be readily separated from the protein without its denaturation, modified by the introduction of substituents, and then rejoined to the apoprotein. Such modifications have been widely used to obtain information about the interaction of the flavin with the protein, mainly from kinetic data—the binding constants, the changes in catalytic activity, and the changes in the electronic and circular dichroism spectra. The 1- and 5-deaza-derivatives or substitution of the methyl groups in the 7- and 8-positions are most often used for such purposes.# Evidently the results obtained cannot as a rule be interpreted unambiguously, since several factors can change simultaneously in the modified compound: the conformations of several aminoacid residues in the active centres (and hence the character of the interactions with the prosthetic group), the steric conditions for the approach of the substrate, and finally, the electronic structure of the isoalloxazine ring itself. Extensive data have been obtained recently on the resonance Raman spectra of modified flavins, both free and bound to different proteins,[65,70,71,103,104] which makes it possible, in principle, to differentiate these factors. It follows from resonance Raman spectroscopic data that the presence of halogen atoms in the 7- and 8-positions changes little the distribution of electron density in the isoalloxazine ring; the changes in the resonance Raman spectra[70] can be accounted for in this instance by the mass effect. However, the introduction of groups containing unshared electron pairs (the hydroxy-, amino-, or mercapto-groups) in these positions leads to radical changes in the resonance Raman spectroscopic parameters (Fig.15). It had been suggested earlier on the basis of UV spectroscopic data (see Massey and Hemmerich[43] and the references quoted therein) that tautomeric (sic) transformations of the type



(I) (II)

i.e. equilibrium between the benzenoid (I) and quinonoid (II) forms, are possible for compounds of this kind. In all cases the bathochromic shift and an increase of the intensity of the long-wavelength absorption band were noted for the suggested quinonoid structure.

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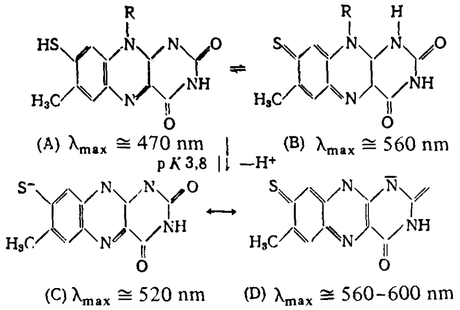
†ETF = electron-transporting flavoprotein.

#In the flavoproteins with known structures,[35,36] the isoalloxazine ring is oriented in such a way that the benzene component and the 7- and 8-methylgroups are on the "surface" and are least in contact with the aminoacid residues of the active centre. This apparently actually accounts for the ease of the binding of the 7,8-modified analogues to the protein.

A large decrease of the frequencies of bands II and III (by 30–40 cm^{-1}), changes in the range 1400–1200 cm^{-1}, and the appearance of a whole series of new bands in the range 1100–1000 cm^{-1} are characteristic of the resonance Raman spectra of these derivatives (Table 5). The changes are especially large in the resonance Raman spectra of 8-mercaptoflavins exhibiting a long-wavelength absorption (λ_{max} = 500–600 nm), greatly exceeding in intensity the absorption by other derivatives (Fig.16). In conformity with UV spectroscopic data, the following tautomeric structures have been proposed for 8-mercaptoflavins as a function of the environment and the ionisation potential:[43]



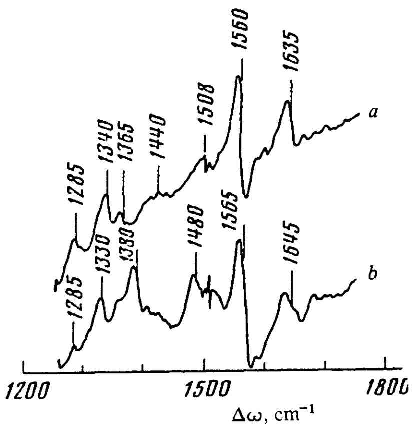


Figure 15. The inverse spectra (resonance excitation) of 8-aminoriboflavin (*a*) and 8-hydroxyriboflavin (*b*) at pH 7.3.[65]

The resonance Raman spectra of mercaptoriboflavin in various states have been obtained.[103] It follows from these data that the frequencies of lines I and II for the protonated form (pH 2) are reduced (by 9 and 14 cm^{-1} respectively relative to the riboflavin), but the constancy of the positions of the remaining lines and, what is more significant, of the distribution of the band intensities indicate the retention of the "benzenoid" character of the electron density, as in the halogeno-derivatives.[70,104] According to resonance Raman data, 8-mercaptoriboflavin[103] and 8-methylmercaptoriboflavin[104] add precisely in this form to the riboflavin-binding protein. The transition to conditions for the formation of the anionic (thiolate) form (C) (accompanied by a bathochromic shift of the absorption band) leads to radical changes in the resonance Raman spectrum, in which the 1616 and 1545 cm^{-1} bands are dominant; the latter band is usually regarded as an analogue of the 1584 cm^{-1} band of the oxidised form, the corresponding vibration being localised in the N(5)–C(4*a*)–C(10*a*) section[67] and it is therefore regarded as an indicator of the double bond character of this fragment.[65,103] The large decrease of the frequency of line II has been interpreted in all investigations as evidence for the decrease of the order of the π-bonds in this section of the isoalloxazine ring and as decisive evidence in support of the quinonoid structures (B) and (D). The study of the variation of the frequency of the 1545 cm^{-1} band[103] has shown that the corresponding normal vibration does indeed contribute to the long-wavelength electronic transition. However, we may note that no convincing evidence has been obtained so far in support of the fact that this vibration is localised in the same fragment as the 1584 cm^{-1} vibration of the oxidised form.

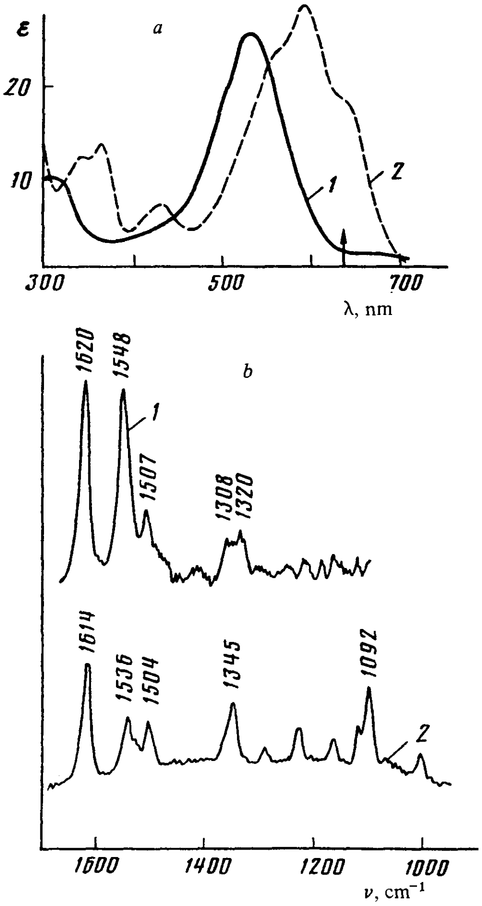


Figure 16. *a*) The electronic absorption spectra of modified flavoproteins: *1*) 8-mercaptoflavodoxin; *2*) D-aminoacid 8-mercapto-oxidase;[43] *b*) the spontaneous resonance Raman spectra: *1*) 8-mercaptoriboflavin (pH 8.4; λ = 514.5 nm); *2*) lactate 8-mercapto-FMN-oxidase (pH 7; λ = 632.8 nm).[65]

It had been noted earlier that the binding of 8-mercapto-FMN by certain proteins does not entail significant changes in the colour of the "red thiolate" form (flavodoxin),[105] while the addition of the modified prosthetic group to lactate oxidase, glucose oxidase, *D*-aminoacid oxidase, and old yellow enzyme results in a change of the red colour to a deep blue colour (Fig.16).[105] Since all the flavoproteins enumerated belong to the class of oxidases, it has been suggested that oxidases stabilise the "blue benzoquinone" structure (D) and that the presence of the aminoacid residue, stabilising the negative charge on the N(1)–O(2) section of isoalloxazine, in the active enzyme centre of the oxidase is essential:

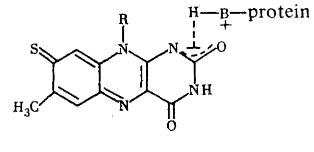


Table 5. The frequencies of the resonance Raman lines (cm^{-1}) of modified flavin systems.

Band designation	RF (Ref.65)[a]	8-OH-RF (Ref.65)[b]	8-OCH$_3$-RBP (Ref 82)	8-SCH$_3$-RBP (Ref.104)	8-NH$_2$RF (Ref.6)	8-NH(CH$_3$)-RBP (Ref.71)	8-N(CH$_3$)$_2$-RF (Ref.65)
I	1631	1635 (1638)	1638	1624	1645	1641	1629
II	1582	1560 (1555)	1578	1564	1565	1567	1558
III	1547	—	1542	1533	—	1537	1519
IV	1501	1508	1506	1505	—	1531	—
V	1462	1440	—	1476	1480	—	—
VI	1407	1365	1413	1405	—	1407	1405
			1387	—	1380	—	1375
VII	1354	1340 (1337)	1358	1348	1330	1360	1335
VIII	1304	—	—	—	—	—	—
IX	1281	1285 (1286)	1276	—	1285	—	1281
X	1250	—	1237	1246	—	—	1251
XI	1228	(1215)	—	—	—	—	1212
XII	1178	—	—	1194	—	—	—
XIII	1161	—	1152	1150	—	1162	1133
XIV	1072	—	1071	1084	—	—	—
				1014	—	—	—

Note. RF = riboflavin; RBP = riboflavin-binding protein.
[a] The discrepancies with the data of Nishina et al.[70] for RBP do not exceed ~2 cm^{-1}. [b] The data of Dutta et al.[71] are given in brackets.

The resonance Raman spectra of the "blue benzoquinone" structures have been obtained by Schopfer et al.[65] (Table 6). The spectrum of 8-mercapto-FMN lactate oxidase excited at λ = 632 nm (denoted by an arrow) is illustrated in Fig.16; the data for glucose oxidase and old yellow enzyme are presented in Table 6. These results demonstrate that the same electronic structure of the 8-mercaptoflavin prosthetic group, differing appreciably from the traditional hydroxy-form of riboflavin, FMN, and FAD, is characteristic of all the proteins enumerated. Certain changes in the frequencies of the principal bands within the limits of each spectrum evidently reflect the specific features of definite protein–flavin interactions in the active centre of the enzyme. In the literature these spectra have been interpreted as referring to the "fully quinonoid" structure (D),[65] while the spectra of derivatives of 8-hydroxy, 8-amino-, 8-mercapto-,[65] 8-methylamino-,[71] 8-methoxy-,[70] and 8-methylthio-riboflavins[104] are thought to be "intermediate" between those corresponding to the typical quinonoid and benzenoid structures with "greater" or "lesser" quinonoid character.[65] Apart from a number of discrepancies (the differences between the resonance Raman spectra of derivatives for which identical "contributions" by the quinonoid structure have been predicted on the basis of electronic spectra,[43,65] a significantly "benzenoid" distribution of intensities in the case of the 8-methoxy- and 8-methylthio-derivatives accompanied by major shifts of band II in the latter case, etc.), the very concept of describing the electronic states as mixtures of resonance structures and of the resonance Raman line shift as a result of a particular "percentage content" of the quinonoid form is unproductive and cannot yield any specific information either about the distribution of electron density in the isoalloxazine ring or about the interactions of the latter with the protein. The correlations of the positions of certain resonance Raman bands with the Hammett constants,[65,104] disregarding the influence of the masses and kinematic interactions on the vibration frequencies (see, for example, the correlations for band I in the study of Schopfer and Morris[104]), are also of little use. Despite the very unique nature of the resonance Raman spectra obtained for modified flavins, they have been scarcely used. The interpretation of these results requires additional experiments with isotope-substituted specimens, which would permit reliable assignments of the vibration frequencies, and also quantum–mechanical calculations of the electron density in the modified flavins.

Table 6. The frequencies (cm^{-1}) in the resonance Raman spectra of 8-mercaptoflavins.[65]

RBP[a]	8-SH-RF[b]	8-SH-FMN-LO[c]	8-SH-FAD-GO[d]	8-SH-FMN-OYE[e]
1631	1620	1614	1606	1611
1582	1548	1536	1530	1528
1547	1507	1504	1501	1500
1501	—	—	—	—
1462	—	—	—	—
1407	—	—	—	—
1354	1360, 1320	1345	1337	1343
1304	—	—	—	—
1281	—	1292	1263	—
1250	—	1223	1209	1220
—	—	—	—	—
1228, 1178, 1161	—	1161	1159	1168
—	—	1110	—	1111
—	—	1092	1099	1087
1072	—	1063	1079	1039

[a] Riboflavin-binding protein, quoted for comparison.
[b] 8-Mercaptoriboflavin, pH 8.4 with added 3 M KI. [c] L-lactate 8-mercapto-FMN-oxidase, pH 7. [d] Glucose 8-mercapto-FAD-oxidase, pH 7. [e] 8-Mercapto-FMN derivative of old yellow enzyme, pH 7.

Stacking Interactions of Flavins. It has been frequently suggested in the literature that the free FMN and FAD groups in solutions exist under certain conditions in the form of stacking complexes. In particular, the changes in the fluorescence properties of flavins have been attributed to interactions of this type. It is known that the fluorescence of FAD in aqueous solution is appreciably quenched compared with an aqueous solution of FMN at the same concentration; it has been suggested[106] that one of the probable causes of the quenching may be the stacking interaction of the isoalloxazine and adenine rings. The possibility of the formation of intramolecular stacked structures from the isoalloxazine and adenine rings in the FAD molecule has been discussed.[107] When 30% of DMSO is added to the solvent, such interaction is significantly weakened and the FAD fluorescence is intensified by a factor of 40, approaching that of FMN. Attempts have been made to detect stacking interactions with the aid of resonance Raman spectra. Comparison of the frequencies in the spectra of aqueous FMN solutions at a concentration of approximately 60 mM,[63] where the FMN molecules should be fully dimerised, with the CALS spectra of dilute aqueous solutions and solutions in the H_2O–DMSO mixture[66] failed to reveal any significant differences. One should note however that these results are difficult to compare, because the data of Nishimura and Tsuboi[63] refer to spontaneous RRS under conditions of virtually non-resonance excitation (λ = 600 nm), while the data of Irvin et al.[66] refer to the excitation of the anti-Stokes ARSS (ω_1 = 495 nm), which gives rise to a negative Lorentzian contour. On comparing the CALS spectra of FAD in water and aqueous DMSO, the authors noted small changes in certain frequencies.[66] However, it was subsequently confirmed that the FMN spectra in solutions at high concentrations, ensuring stacking interactions (> 50 mM), do not differ from the spectra of dilute solutions (< 2 mM).[64]

Flavocytochromes. These compounds, which function in electron transport chains, contain two centres for oxidation-reduction reactions: flavin and cytochrome (haem group). The mechanism of the functioning of flavocytochromes is in many respects still obscure;[108] little is known also about an interesting feature of these compounds—the postulated intramolecular tunnelling from flavin (electron donor) to cytochrome (electron acceptor). Furthermore, the study of this interaction is of general importance for many-centre enzymes.

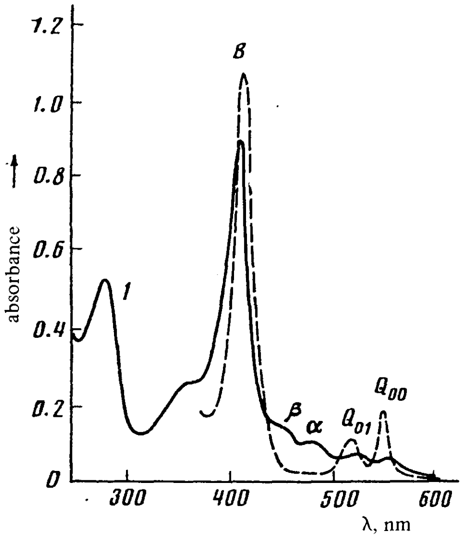


Figure 17. The electronic absorption spectra of flavocytochrome c_{552} in the oxidised (curve *1*) and reduced (curve *2*) forms; the symbols *B*, Q_{01}, and Q_{00} denote the absorption bands of haem c and α and β denote the absorption bands of the flavin component.[113]

Flavocytochrome c present in purple and green phototropic bacteria, which play an important role in the biological reduction of sulphates and in the general sulphur turnover on Earth, has been most thoroughly investigated in the class of cytochromes.[39] Flavocytochrome c_{552}, isolated from *Chromatium vinosium*, consists of two non-equivalent subunits, one of which (M_r = 21 000) contains two haem *c* groups, while the other (M_r = 46 000) contains one FAD group.[109] The isoalloxazine ring is in this case covalently bound to the protein by a sulphide linkage in the 8-position.[110] According to EPR data,[111] the two haem c groups are non-equivalent; the immediate environment of one of these groups (apparently consisting of the ligands) varies with the pH.

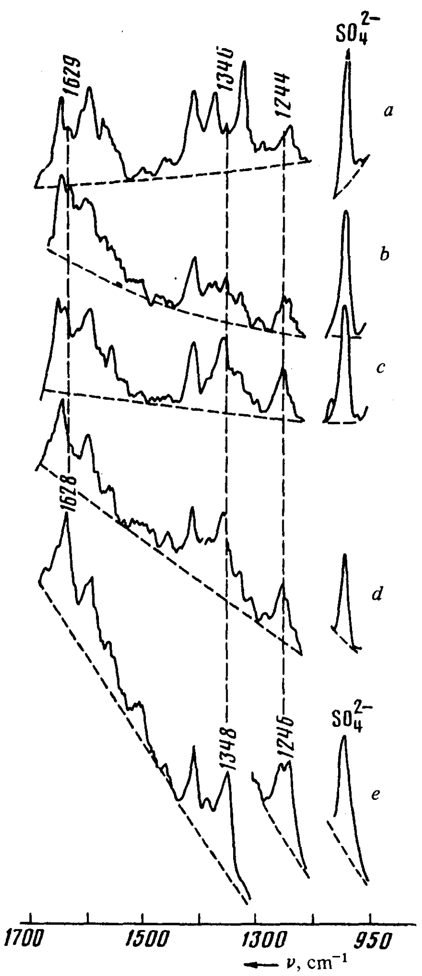


Figure 18. The resonance Raman spectra of flavocytochrome c_{552} (pH 6.5) on excitation with light corresponding to the 514.5 (*a*), 501.7 (*b*), 496.5 (*c*), 488.0 (*d*), and 476.5 nm (*e*) lines; internal standard—SO_4^{2-} ion (ν = 983 cm^{-1}); the vertical dashed lines indicate the positions of the resonance Raman lines of flavin.[113]

Flavocytochrome c_{552} has been investigated by the resonance Raman method simultaneously by two groups of investigators.[112,113] Owing to the unsuccessful choice of the exciting frequencies in the study of Ondrias et al.,[112] it was not possible to identify the resonance Raman lines which could be assigned to the isoalloxazine rings. The electronic absorption spectrum of the enzyme (Fig.17) consists of a superposition of the intense absorption by haem [the *B* bands (Soret bands) Q_{00} and Q_{01}] and less intense bands at approximately 450 and 480 nm referring to the flavin fragment. By altering the frequency of the exciting line, the authors[113] isolated the 1629, 1346, and 1244 cm^{-1} lines of the isoalloxazine ring together with the intense resonance Raman lines of the cytochrome at 1645, 1566, and 1366 cm^{-1}, which are close to the frequencies observed for horse ferricytochrome c (1637, 1563, and 1316 cm^{-1} respectively[114]). The intensity of the isoalloxazine lines is highest on excitation at λ = 476.5 nm, in the region of the bands due to the electronic transitions of flavin (Fig.18).

The resonance Raman spectrum of the reduced (ferro) form of flavocytochrome c_{552} contains lines referring exclusively to the haem groups;[113] their number, polarisation, and frequencies are virtually the same as for other ferrocytochromes c.[115] Judging from the symmetrical contours of the sharp 1588 and 1316 cm^{-1} lines, both haem groups in the ferrocytochrome c_{552} molecule should be identical. The absence of bands due to the isoalloxazine ring shows that the flavin exists in this case in the fully reduced form and not in the semiquinone form.[113]

The photoreduction of the entire enzyme and its constituent cytochrome- and flavin-containing submits separately as well as the interaction with strong inhibitors (sulphite and cyanide) have been investigated with the aid of RRS.[113] The changes in the intensities of the resonance Raman bands in the spectra of the complexes with cyanide and sulphite suggest that both adducts are formed as a result of the addition to the N(5) atom of the isoalloxazine ring, which is the cause of the inhibition of the enzyme. It has been shown[113] that in the photoreduction, which in this case proceeds exclusively in the presence of ethylenediaminetetra-acetic acid, the first prosthetic group to be reduced is the flavin system, while the haem groups cannot be reduced in the absence of flavin. These experiments constitute the first direct evidence for the occurrence of intramolecular transfer from the flavin group to the cytochrome in this class of enzymes.

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Thus extensive data have now been obtained on the resonance Raman spectra of flavins. Evidently the method can be used successfully for the identification of the isoalloxazine ring and the derivation of information about its structure in all possible oxidation and ionisation states. Under conditions where the scope of NMR is extremely limited, resonance Raman spectroscopy remains in essence the only method potentially capable of yielding extensive information about the ground and excited states of flavin systems. Nevertheless, these data have so far been used to a small extent. Compared with the novel methods of isolation and synthesis of, for example, the modified specimens and with the exceptionally sophisticated experimental spontaneous and non-linear resonance Raman spectroscopic technique, the results of the interpretation appear to be modest. This situation is caused mainly by the inadequate development of the theoretical basis of the analysis of the normal vibrations and quantum-mechanical calculations of the electron density in model flavin systems. Evidently the description of the changes in the electronic states of the isoalloxazine ring in terms of the percentage contents of the resonance structures cannot promote the discovery of the real situation. Despite the abundance of data available on isotope-substituted specimens and modified systems, there has been so far no adequate calculation for the normal vibrations of flavin. In view of the quantum-chemical and vibrational spectroscopic methods which have now been developed and the present level of computational techniques, such theoretical data could be readily obtained after the correct choice of model. All the information about the frequencies, intensities, and polarisations of the resonance Raman lines could be fully employed on this basis in order to deduce the state of the isoalloxazine ring and its interactions with the protein environment.

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Progress in the Polymer Chemistry of Borates

B.P.Tarasevich and E.V.Kuznetsov

Using a combined approach based on the symbiosis of macromolecular and colloid chemistry of polymers with inorganic chemistry, data on the low- and high-molecular-weight anionic metal oxoborates in the crystalline, amorphous, and vitreous states, in solution, in the melt, and in the gas phase are surveyed. An attempt is made on this basis to present an adequately logical and well-founded picture of their structure, to indicate a new method of study, and to facilitate the prediction of the properties of technical materials and the improvement of the technology of their manufacture. The entire wide variety of borates and many of their properties can be accounted for by the variation of the configurations and conformations of the macroanions in response to changes in external influences as a result of the flexibility of the B-O-B bonds by virtue of the O atoms being in a state intermediate between sp^2- and sp-hybridisation involving B atoms. The necessity to develop the polymer chemistry of compounds with the E-O-E linkages (E = B, Si, P, Al, etc.) is emphasised. It is noted that the chemistry of macroanions is in the forefront in this respect.

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I. INTRODUCTION

The unity of the nature of organic, organoelemental, and inorganic polymers and the differences between them have already been discussed in a review,[1] where the inadequate development of this problem in relation to polymers of the last type was noted. The number of new publications on this topic can be literally measured in single figures.[2,3] This is clearly inconsistent with the abundance and importance of inorganic polymers in nature and technology.[4–8] The ideas developed in a monograph by Korshak et al.[9] stimulated at an earlier stage the consideration of certain aspects of the macromolecular physics and chemistry of boron oxides and hydrogen oxoborates.[1] This review is devoted to polymeric metal oxoborates[†] (henceforth referred to simply as borates).

[†] The fluoro-, peroxo-, and other borate systems as well as inorganic polymers with B—O—E linkages in the macroanions (E = Si, Al, P, etc.), i.e. the corresponding boroelementoxanes,[10] will not be considered here. We note only that the use of the principles of macromolecular chemistry will permit an approach to the synthesis of such polymers and materials based on them.[11–16]

The characteristic features of the electronic structure of boron are responsible for the presence of the BO_3 and BO_4 sp^2- and sp^3-hybrids in the structures of borates and also for the possibility of their interconversions.[17] This complicates the structure of borates compared with, for example, phosphates[18] or silicates.[19] The elucidation of the structures of many borates has been scarcely reflected in their terminology, particularly in the trivial names of natural compounds. Although stereoregular crystalline linear (chain and cyclochain) borate polyanions can be fully described, according to IUPAC recommendations,[20] with the aid of stereochemical definitions and designations adopted by IUPAC for polymers,[21] in practice such terminology is not being used. Since the existing nomenclature for polymers[20–22] refers solely to linear single-stranded and quasi-single-stranded structures, the present review has retained mainly the traditional terminology of the chemistry of borates, in particular, the prefixed "phyllo" and "tekto" are used to designate two- and three-dimensional structures respectively.[23] Since the term "polyanion" has a dual significance in the chemistry of borates—it is frequently used to designate both intrinsically polymeric (chain, layer, and network) and isolated ("island") anions with a low degree of polymerisation, in the present review the latter are referred to as oligoanions[24] and the former as macroanions. The macroanions are in their turn subdivided into linear (poly-), layer (phyllo-), and network (tekto-). Instead of terms of the type "basic structural blocks",[25] "basic structural units",[26] etc., the term "constitutional repeat units" (CRU) [27] (it is also referred to as the elementary unit[28]), taken from the chemistry of macromolecular compounds, is used. The symbol "∞" has been replaced by the designation "n" used in the chemistry of macromolecular compounds.

The oligoanions are subdivided, as usual, into triborate, tetraborate, pentaborate, etc. anions. In order to reflect their wide variety, caused by the different combinations of BO_3 and BO_4 for the same number of boron atoms, it is most convenient to employ the nomenclature of complex compounds.[29] The review includes data on oxoborates published up to 1985, including data on new oligoanions with $n = 12$ [30] and $n = 16$,[31] on the heptaborate CRU,[32] etc., for example, the structure $CaO.2B_2O_3.0.5H_2O$,[33] which have not been included in any of the previous reviews.[34] Data on anhydrous crystalline[26] and vitreous[7,35] borates, etc. have also been supplemented.

II. HYDRATED BORATES

1. Crystalline Compounds

The fundamental principles governing the formation of structures[25] are described below taking into account the postulates of the chemistry of macromolecular compounds:

1. The simplest groups in the structures are BO_3 and BO_4.
2. The monomeric and dimeric anions are made up only of BO_3 groups or only BO_4 groups.
3. As a result of oligocondensation, the monomeric anions tend to form reactive anionic preoligomers, in which the degree of polymerisation of the simplest groups BO_3 (BO_4), functioning as structural fragments (subunits[20]) of the oligoanions, is $n \geq 3$.
4. The oligoanions specified in paragraph 3 can be modified by grafting to them side branches consisting of boron–oxygen and other element–oxygen groups.
5. Both monomeric and oligomeric anions (including modified anions) can polymerise via polycondensation (sometimes with ring opening) to macroanions functioning at the given stage of structural organisation as the CRU of the macroanions.#
6. In the structures of hydrated borates there is a possibility of the coexistence of the macroanions with mono-, di-, and oligo-anions.
7. In the hydrated borates, the oxygen atoms capable of being protonated are usually (but not always) protonated in the following sequence: initially the terminal oxygen ions (with formation of hydroxy-groups), next the oxygen atoms of the BO_4 sp^3-hybrid, then the oxygen atoms of the BO_3 sp^2-hybrid, and finally the hydroxy-group (with formation of water molecules).

The water in the crystalline hydrated borates can be present both in the molecular form (five classes of such water are distinguished)[36] and in the form of protons and hydroxyls, the hydrogen bonds playing an important role in the formation of the structures under these conditions. As the water content diminishes, the degree of polycondensation and the degree of cross-linking of the boron–oxygen anions increase.[36]

Fig.1 presents the known varieties of the borate mono-, di-, and oligo-anions in the fully hydrated form. Partly dehydrated forms have also been detected in real borates. Some of the oligomers illustrated in Fig.1 (*D*, *a*; *G*; *H*) have so far been detected in a modified form and as CRU of the macroanions. Examples of similar modified CRU are presented in Fig.2.

Fig.3 illustrates the "pentamer trimer" (i.e. a tripentaborate—not a pentadecaborate), found in the structure of natural ammonioborite,[37] and also the oligoanion $[B_{16}O_{24}.(OH)_{10}]^{10-}$ in which there are two heptaborate anions held by the BO_3 triangles.[31] The last example can also be regarded as an exception to the 7th of the principles quoted above; in the presence of water molecules, non-protonated oxygen bound to boron is present in the structure.

Starting with triborates ($1BO_3 + 2BO_4$), stereoisomers begin to appear. The triborate ring is a component of almost all oligoanions [the central O atom in the structure of the hexamers is coordinated to three B atoms at once and the charge of the hexamers is not equal to the number of B(IV) atoms as in other oligoanions, where it is smaller by unity]. One of the varieties of the tetraborate compounds is an exception.

The stereochemical similarity of borates to organic compounds has already attracted the attention of investigators[38] and Fig.3*b* demonstrates their ability to form "chelate" complexes which constitute the basis of many coordination polymers.[39]

Examples of borates in the macroanions of which the residues of mono- and oligo-anions behave as CRU are given in Tables 1 and 2. Figs.4 and 5 represent the fragments of certain macroanions included in the above Tables.

The set of data presented reveals the wide variety of macroanions, the origins of which are discussed in Section IV. In the light of ideas about the functionality of monomers in polycondensation,[76] the tendency towards the formation of predominantly heterocyclochain and layer polyboroxane macroanions, the possibility of their successive cross-linking, and also the possibility of the formation of

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#The macroanions are capable of forming still higher forms of supermolecular (more precisely, "superionic") structural organisation, for example, formations of the spherulite type.

statistical and block-copolymers with B—O—E linkages (E = Si, Al, P, etc.) were already considered previously.[1] The possibility of the modification of the structures illustrated in Fig.1 by the grafting of various side branches and the formation of the CRU shown in Fig.2 also follows from the same pre-conditions. This type of transformation occurs likewise in the case where the polycondensation of the oligoanions is accompanied by the opening of the ring, as happens, for example, in the conversion of borax into kernite in accordance with the scheme shown in Fig.6.[25]

It is noteworthy that polyborates [for example, hydroboracite (III) and colemanite (IV) in Table 1] frequently give rise to superionic formations of the type of spherulites,[77] despite the views of Frenkel'.[6]

Since boron absorbs effectively slow neutrons and hydrogen absorbs fast neutrons,[78] hydrated borates and binding compositions based on them[79,80] are promising as materials for protection against neutron radiation. The mechanical indices (density, hardness, etc.) increase almost linearly on passing from the monoanionic to the di- and oligo-anionic structures and further to polymers, reaching a maximum for network macroanions.[81] The latter also contain the maximum amount of boron but the hydrogen content is then reduced to a minimum. This means that chain or layer macroanions have the optimum properties. An idea about the necessary ratio of the components can be gained from the data in Tables 1 and 2. On the other hand, the conditions in the synthesis of the binding materials must be close to those in the synthesis of single crystals (see the original communications quoted in the Tables). Clearly polycrystalline and even amorphous polymers, formed by borates at 323—523 K,[17] are suitable for the preparation of technical binders, phylloanions being usually produced under hydrothermal conditions.[82] It is useful to employ for this purpose

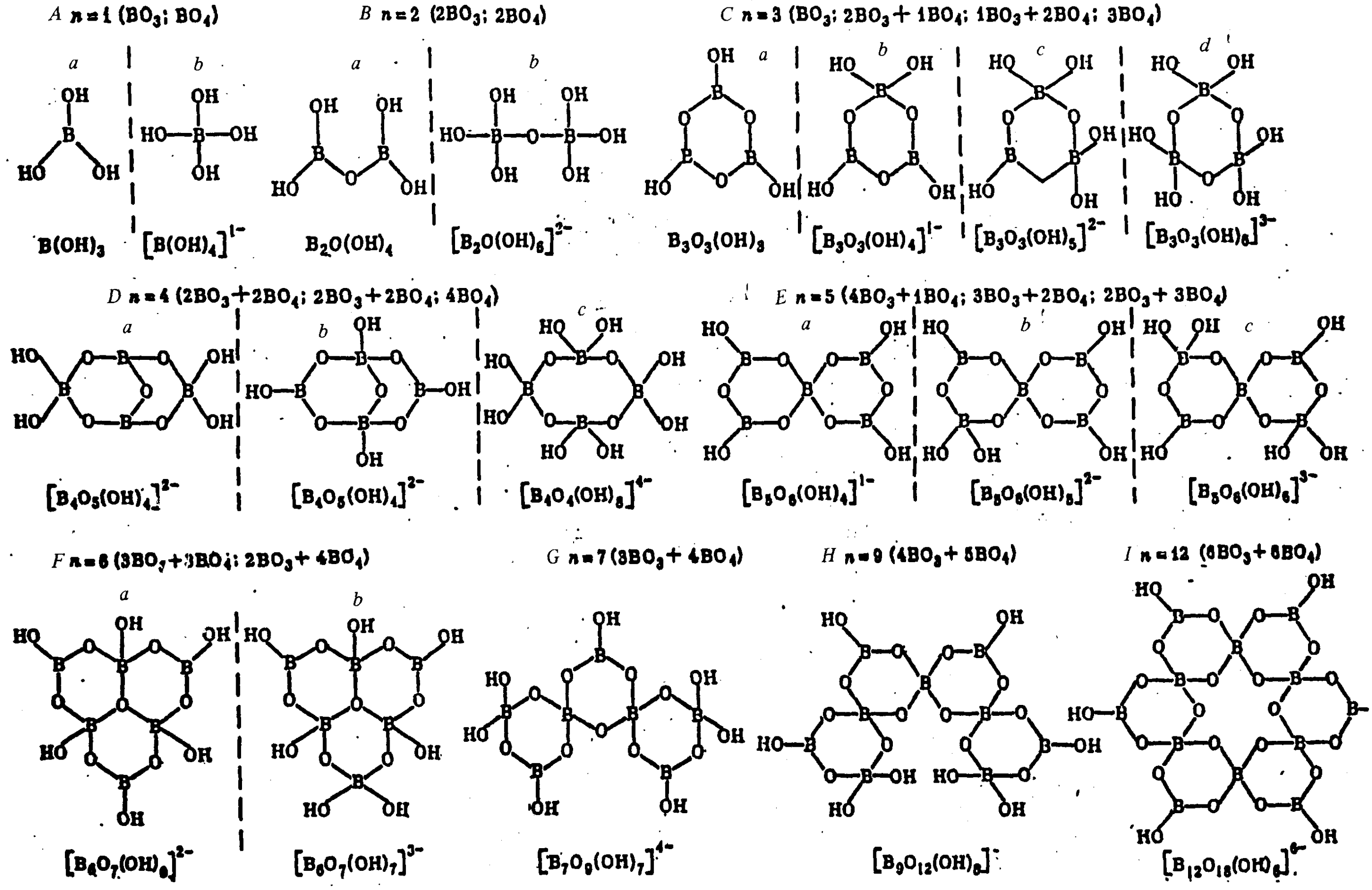
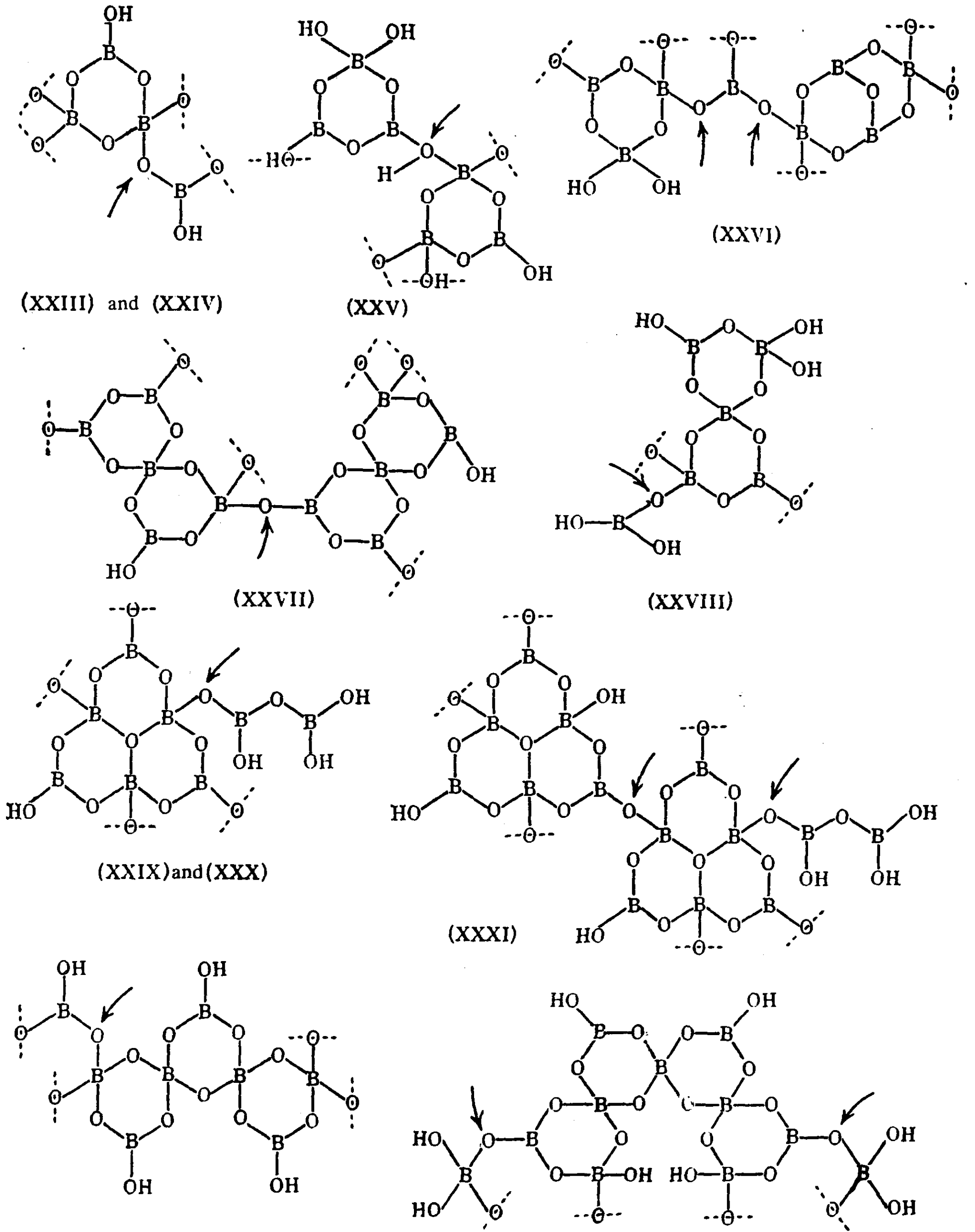


Figure 1. Borate monomers, dimers, and preoligomers with $n \geq 3$ in the fully hydrated form; their residues occur as the "usual" CRU of macroanions (Table 1) and subunits of modified (combined) CRU (Fig.2).

the experience gained in the chemistry of macromolecular compounds in carrying out the polycondensation reactions[83] and to invoke the mechanochemical reactions[84] which are already employed in the practical synthesis of borates.[85]

Hydrated borates, for example calcium borates, are manufactured on an industrial scale.[86] The B_2O_3 content in the polymeric borates is higher than in the monomeric and oligomeric borates and for this reason, in the manufacture of calcium borates, the half-finished product $CaO.B_2O_3.6H_2O$ with the monoanion $[B(OH)_4]^-$ [34] is nowadays subjected to polycondensation in the course of the so called "drying" (Ref.86, p.115) and is converted into the commercial product $CaO.B_2O_3.2H_2O$ (43% B_2O_3). Commercial preparations with a higher B_2O_3 content can be obtained under conditions where the degree of polymerisation of the boron–oxygen anions is increased further.


(XXIII) and (XXIV)

(XXV)

(XXVI)

(XXVII)

(XXVIII)

(XXIX)and(XXX)

(XXXI)

(XXXII)

(XXXIII)

Figure 2. Examples of modified CRU in the macroanions of hydrated borates (the numerals correspond to those adopted in Table 2 for specific compounds); the arrows indicate the sites of grating of subunits; the connecting oxygen atoms shared with neighbouring CRU are indicated by dashed lines (see the footnote to Table 2).

The adhesive, binding, and film-forming properties of borates,[87, 88] which are characteristic of polymers and are considered in the next Section, are also of practical interest.

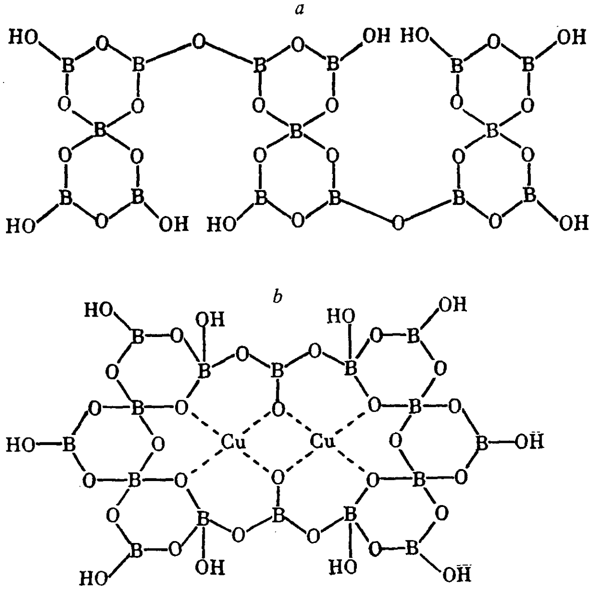


Figure 3. The tripentaborate oligoanion (*a*) in natural ammonioborite $(NH_4)_3[B_{15}O_{20}(OH)_8]\cdot 4H_2O$ and the oligoanion with $n = 16$ (*b*) as part of the "chelate" oligoanion in synthetic $Na_6\{Cu_2[B_{16}O_{24}(OH)_{10}]\}\cdot 12H_2O$.

2. Solutions of Oxoborates

The water-soluble borates of Group Ia s elements have been most thoroughly investigated. On dissolution in water, their macroanions are degraded as far as the formation of mono-, di-, and oligo-anions with $n = 3$–5.[1] The regions in which some of them predominate in solution are shown in Fig.7.[34,82]

It is striking that the structures made up wholly of BO_4 tetrahedra (for example, the network HBO_2-I macromolecules[1]) hydrolyse very slowly, in contrast to structures containing also the BO_3 triangles (for example, the cyclo-chain HBO_2-II macromolecules[1]), which makes it possible to isolate them from the mixture.[89] Consequently the resistance of borate macroanions to hydrolysis can be increased by filling with electrons the unoccupied *p* orbitals of the BO_3 sp^2-hybrids by their interaction with electron density donors, for example, with phosphates,[7,15] or by exposing them to UV [13] or ionising [90] radiation and by similar procedures.

Highly concentrated solutions in the M_xO_y–B_2O_3–H_2O systems (M = metal),[87,88] obtained on heating or hydrothermal treatment, exhibit adhesive, binding, and film forming properties. Concentrated solutions in the M_2O–B_2O_3–SiO_2–H_2O system have the same properties.[91] In the latter case even a very small content of boron compounds in compositions made up of oxygen compounds induces qualitative changes in the structures and properties of the statistical and block-copolymers formed.[91]

As already mentioned,[1] true solutions of borate polymers can be most readily obtained in non-aqueous solvents—either organic such as nitrobenzene in which they swell [92] or in "water removing" inorganic solvents of the type of H_2SO_4.[93] It has been suggested that in the latter case dissolution is

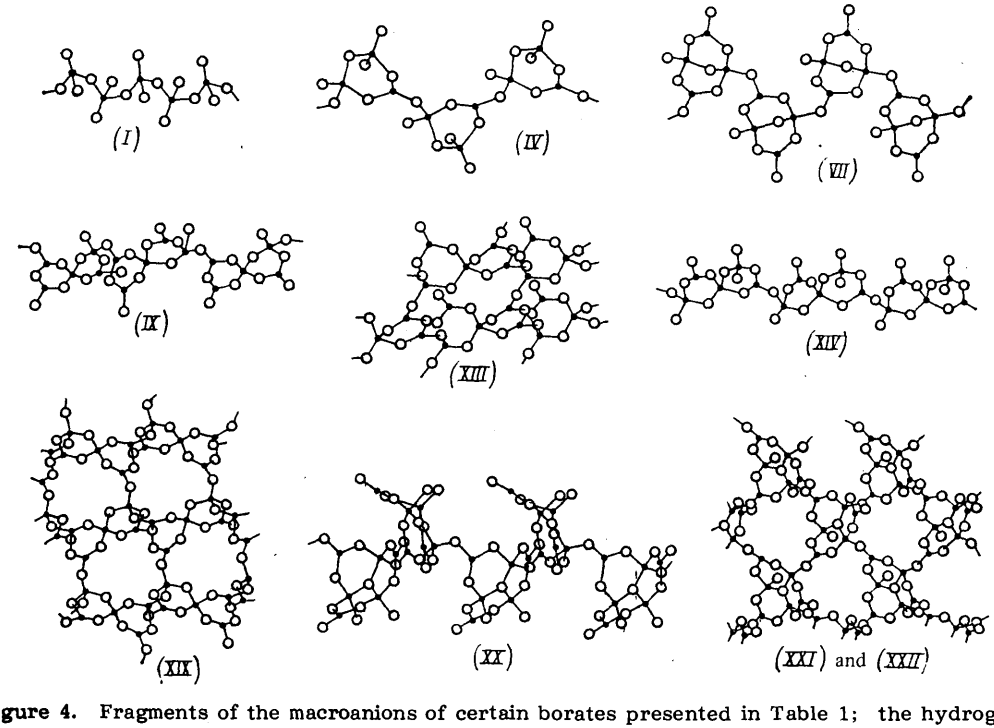
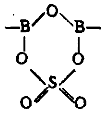
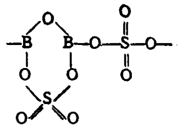


Figure 4. Fragments of the macroanions of certain borates presented in Table 1; the hydrogen atoms in the hydroxy-groups have been omitted for simplicity; here and henceforth the small filled circles denote boron and the larger open circles denote oxygen.

accompanied either by complex formation[94] or by polymer-analogue transformations with formation of CRU of the type[95]



or



The formation of a complex between $B(OH)_3$ and iron salts in solutions has also been noted.[96]

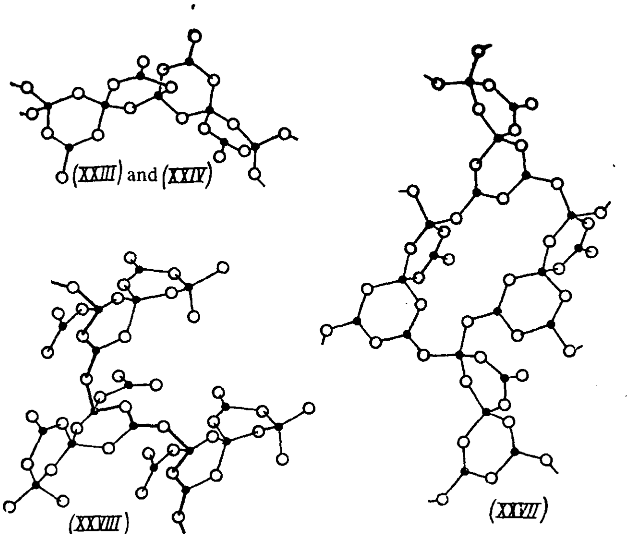


Figure 5. Fragments of the macroanions of certain borates presented in Table 2.

The set of data presented above provides a key to the understanding of the genesis of natural borate ores and the determination of the necessary conditions for the preparation of their synthetic analogues.

In nature at $T < 323$ K, mono-, di-, and oligo-borates are produced in the primary sedimentation period, undergoing various kinds of changes in the subsequent post-sedimentation period. As a result of polycondensation in accordance with the scheme[38]

$$[B_xO_y(OH)_z]^{(2y+z-3x)-} \xrightarrow[-qHOH]{t^\circ} [B_xO_{y+1}(OH)_{z-2}]_{q+1}^{(2y+z-3x)-} ,$$

accompanied under suitable conditions by ring opening (Fig.6), the grafting of side groups, and similar processes, the primary sedimentation borates are usually converted into secondary, post-sedimentation borates, as a rule chain or layer borates, following a change in thermodynamic conditions in deep layers.[82]

In order to obtain a synthetic borate with a particular structure, it must be deposited from a solution containing definite mono- or oligo-anions. On the other hand, as can be seen from the data in Fig.7, each of them exists predominantly within narrow temperature, pH, and concentration ranges, in the presence (see Section IV) of particular metal cations, and, finally, within a limited time interval (on "ageing" of the solutions). This greatly complicates the separation of borate homologues, which requires the application of many sophisticated technological methods and special procedures.[34,86,97–99] On the other hand, if the solution contains borate homologues of several varieties at once, then non-crystalline variable-composition amorphous borates are deposited from such a solution.

3. Amorphous Systems—Behaviour on Heating

Apart from the procedure noted above, amorphous borates are also formed in the course of the dehydration of crystalline hydrated borates (at a temperature ensuring the removal of the most strongly bound OH groups from the structures), yielding the so called amorphous powders.[77] The conversion of the amorphous borates into crystalline anhydrous compounds on further heating is accompanied by an effect which has been called the "borate rearrangement" (BR).[77]

In contrast to the usual crystallisation, whose rate is limited by the rate of removal of energy from the system, BR has an explosive (chain) exothermic character and occurs always at a reproducible temperature specific to each borate

Table 1. Examples of polymeric hydrated crystalline borates with the "usual" CRU (see also Figs.1 and 4).

CRU[a] of macroanions	Initial monomer or preoligomer	Form and formula of macroanions	Examples of specific compounds (the trivial names are also quoted for the natural borates)	Refs.	Designation
Monoborate	$[B(OH)_4]^{1-}$	Chain $[B^{IV}O(OH)_2]_n^{n-}$	Wimsite $Ca[BO(OH)_2]_{2n}=CaO\cdot B_2O_3\cdot 2H_2O$	[40]	(I)
Triborate	$[B_3O_3(OH)_4]^{1-}$	Cyclochain $[B_2^{III}B^{IV}O_4(OH)_2]_n^{n-}$	$Tl[B_3O_4(OH)_2]_n\cdot 0{,}5H_2O=Tl_2O\cdot 3B_2O_3\cdot 3H_2O$	[41]	(II)
		Cyclochain $(B^{III}B_2^{IV}O_4(OH)_3]_n^{2n-}$	Hydroboracite $CaMg[B_3O_4(OH)_3]_{2n}\cdot 3H_2O = CaO\cdot MgO\times$ $\times 3B_2O_3\cdot 6H_2O$	[42]	(III)
	$[B_3O_3(OH)_5]^{2-}$		Colemanite $Ca[B_3O_4(OH)_3]_n\cdot H_2O=2CaO\cdot 3B_2O_3\cdot 5H_2O$	[43]	(IV)
		Layer $[B^{III}B_2^{IV}O_5(OH)]_{nn}^{2nn-}$	Fabianite $Ca[B_3O_5(OH)]_{nn}=2CaO\cdot 3B_2O_3\cdot H_2O$ (mono lin.)	[44]	(V)
			$Ca[B_3O_5(OH)]_{nn}=2CaO\cdot 3B_2O_3\cdot H_2O$ (orthorhomb.)	[45]	(VI)
Tetraborate[b]	$[B_4O_5(OH)_4]^{2-}$	Cyclochain $[B_2^{III}B_2^{IV}O_6(OH)_2]_n^{2n-}$	$Na_2[B_4O_6(OH)_2]_n=Na_2O\cdot 2B_2O_3\cdot H_2O$	[46]	(VII)
Pentaborate	$[B_5O_6(OH)_4]^{1-}$	Cyclochain $[B_4^{III}B^{IV}O_7(OH)_2]_n^{n-}$	Larderellite $NH_4[B_5O_7(OH)_2]_n\cdot H_2O=2NH_4OH\cdot 5B_2O_3\cdot 3H_2O$	[47]	(VIII)
		Cyclochain $[B_3^{III}B_2^{IV}O_7(OH)_3]_n^{2n-}$	Escurite $Na_2[B_5O_7(OH)_3]_n\cdot 2H_2O=2Na_2O\cdot 5B_2O_3\cdot 7H_2O$	[48]	(IX)
		Layer $[B_3^{III}B_2^{IV}O_8(OH)]_{nn}^{2nn-}$	Nasinite $Na_2[B_5O_8(OH)]_{nn}\cdot 2H_2O=2Na_2O\cdot 5B_2O_3\cdot 5H_2O$	[49]	(X)
	$[B_5O_6(OH)_6]^{3-}$		$K_2[B_5O_8(OH)]_{nn}\cdot 2H_2O=2K_2O\cdot 5B_2O_3\cdot 5H_2O$	[50]	(XI)
		Ditto in combination with monomeric $B(OH)_3$ located in the plane of the layers[c]	Gowerite $Ca[B_5O_8(OH)]_{nn}B(OH)_3\cdot 3H_2O=CaO\cdot 3B_2O_3\cdot 5H_2O$	[51]	(XII)
			p- and A-Witchites $Sr_2[B_5O_8(OH)]_{2nn}\cdot B(OH)_3\cdot H_2O = 4SrO\times$ $\times 11B_2O_3\cdot 7H_2O$	[52, 53]	(XIII)

Table 1 (cont'd).

CRU[a] of macroanions	Initial monomer or preoligomer	Form and formula of macroanions	Examples of specific compounds (the trivial names are also quoted for the natural borates)	Refs.	Designation
Pentaborate	$[B_5O_6(OH)_6]^{3-}$	Cyclochain $[B_2^{III}B_3^{IV}O_7(OH)_4]_n^{3n-}$	Probertite $NaCa[B_5O_7(OH)_4]_n \cdot 3H_2O = Na_2O \cdot 2CaO \cdot 5B_2O_3 \times \times 10H_2O$	[54]	(XIV)
		Layer $[B_2^{III}B_3^{IV}O_8(OH)_2]_{nn}^{3nn-}$	Heydornite $Na_2Ca_3Cl(SO_4)_2[B_5O_8(OH)_2]_{nn}^{d}$	[55]	(XV)
			$Na_3[B_5O_8(OH)_2]_{nn} \cdot H_2O = 3Na_2O.5B_2O_3.4H_2O^{d}$	[56]	(XVI)
			$Li_3[B_5O_8(OH)_2]_{nn} = II = 3Li_2O \cdot 5B_2O_3 \cdot 2H_2O$ (orthorhomb.)[e]	[57]	(XVII)
		[f]Network $[B_2^{III}B_3^{IV}O_9]_{nnn}^{3nnn-}$	Hilgardite $Ca_2[B_5O_9]_{nnn} \cdot Cl \cdot H_2O = 3CaO \cdot CaCl_2 \cdot 5B_2O_3 \times \times 2H_2O$(monoclin.)[g]	[58]	(XVIII)
			$Na_3[B_5O_9]_{nnn} \cdot H_2O = 3Na_2O \cdot 5B_2O_3 \cdot 2H_2O$	[59]	(XIX)
Hexaborate	$[B_6O_7(OH)_6]^{2-}$	Cyclochain $[B_3^{III}B_3^{IV}O_8(OH)_4]_n^{2n-}$	Aristarainite $Na_2Mg[Ba_6O_8(OH)_4]_{2n} \cdot 4H_2O = Na_2O \cdot MgO \times \times 6B_2O_3 \cdot 8H_2O$	[60]	(XX)
		Layer $[B_3^{III}B_2^{IV}O_9(OH)_2]_{nn}^{2nn-}$	Nobleite $Ca[B_6O_9(OH)_2]_{nn} \cdot 3H_2O = CaO \cdot 3B_2O_3 \cdot 4H_2O$	[61]	(XXI)
			Tanellite $Sr[B_6O_9(OH)_2]_{nn} \cdot 3H_2O = SrO \cdot 3B_2O_3 \cdot 4H_2O$	[61]	(XXII)

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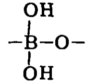
[a] The CRU of the macroanions[27] may not be identical with the stereorepeating unit.[21] Thus the CRU in wimsite I is



$-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{B}}-O-$

, while the stereorepeating unit is in essence a diborate unit consisting of two BO_4 tetrahedra.[40]

[b] See also Table 2 [(XXIII) and (XXXIV)].

[c] The monomeric $B(OH)_3$ groups in gowerite are located in each layer, while in p- and A-witchites they are located in alternate layers. In the structures of the latter the two-layer arrangements made up of identical phylloanions differ only by their relative dispositions; whereas the first layers are identical, the second in A-witchite is a mirror image of the second layer of p-witchite in the plane perpendicular to the c axis.[62]

[d] Although compounds (XV) and (XVI) have the same initial preoligomer $[B_5O_6(OH)_6]^{3-}$, its polycondensation can occur with participation of different OH groups, so that ultimately the end groups in compound (XV) consist of two different triangles with one OH group in each, while those in compound (XVI) consist of two OH groups in one of the tetrahedra.

[e] The synthesis under a pressure of about 100 MPa results in the formation of $Li_3[B_5O_8(OH)_2]$-I (tetragonal), in the anionic network of which it is possible to distinguish helical strips made up of triborate rings ($1BO_3 + 2BO_4$).[63] Sections through the deformation electron density of this borate[64] indicate the covalent character of the boron–oxygen bonds in the BO_3 and BO_4 groups and also in the B–O–B bridges, whereas the Li–O bonds are significantly ionic.

[f] The tektoanion is anhydrous and contains no functional OH groups, being a product of a later stage of the three-dimensional polycondensation of the preoligomer $[B_5O_6(OH)_6]^{3-}$. The zeolite-like boron–oxygen skeleton formed has large cavities in which water molecules are accommodated and in the case of compound (XVIII) also chlorine, so that the borates (XVIII) and (XIX) constitute, as it were, an intermediate stage on the way to the fully anhydrous systems—see (LXII) and (LXIII) in Table 3. Having the same CRU, the macroanions of (XVIII) and (XIX) nevertheless consist of different stereorepeating units: in compound (XVIII) the identity period along the boron–oxygen chains in the network is 0.63 nm, while in compound (XIX) it is 1.12 nm, i.e. corresponds to 2CRU.

[g] The triclinic modification of hilgardite has the same tektoanion.[65]

(somewhat below melting point T_m), and is accompanied by a marked contraction, an increase in the density and hardness of the substance, so that, on the basis of physical properties, it is difficult to put forward the hypothesis that before and after BR one is dealing with a substance having the same chemical composition.[77] It has been established[100–103] that, above the temperature of the BR exothermic effect, the specimens consist as a rule of a mixture of two borates, for one of which the modulus $m = B_2O_3/M_xO_y$ is higher and for the other lower than for the initial borate—in the limit it is made up of B_2O_3 ($m = \infty$) and monomeric (dimeric) borates with a minimum modulus if the newly formed borates are thermodynamically unstable. From the standpoint of the chemistry of macromolecular compounds, this resembles very closely the solid-phase polycondensation[104] or polymerisation[105] reactions. Both reactions proceed at an appreciable rate over a narrow temperature range below T_m, are autocatalytic, their rate has a high temperature coefficient, and their activation energy is also high. Bearing in mind that at the instant of the occurrence of the BR amorphous borates already lack the OH functional groups[100–103]§ (although the isolation of low-molecular-weight anionic products in the chemistry of silicates is also attributed to polycondensation processes as an alternative to ionic polymerisation[107]), it is more likely that the BR represents a kind of unusual solid-phase polymerisation process. It is noteworthy that, in the course of the BR, a fundamental change in the structures of the CRU of the macroanions frequently takes place. For example, colemanite, (IV) in Table 1, is converted after the BR into a mixture of $Ca[(BO_2)_2]_n$, (XXXV) in Table 3, and $Ca_2[B_6O_{14}]_{nnn}$, (LXXVI) in Table 4,[102] while hydroboracite, (III) in Table 1, is converted into a mixture of $Ca[(BO_2)_2]_n$

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§ Certain iron borates are exceptions.[106]

Table 2. Examples of polymeric hydrated crystalline borates with modified (combined) CRU (see also Figs.2 and 5).

Initial monomers and oligomers whose grafting results in the formation of the subunits in the CRU	Form and formula of macroanion[a]	Examples of specific compounds (the trivial names of the natural borates are also given)	Refs.	Designation
$(2BO_3 + 2BO_4)$[b]	Cyclochain $[B^{III}B^{IV}_2O_5(OH)\cdot B^{III}O(OH)]^{2n-}_n$	Kernite $Na_2[B_4O_6(OH)_2]_n\cdot 3H_2O{=}Na_2O\cdot 2B_2O_3\cdot 4H_2O$ $Tl_2[B_4O_6(OH)_2]_n\cdot 2H_2O{=}Tl_2O\cdot 2B_2O_3\cdot 3H_2O$	[66] [67, 68]	(XXIII) (XXIV)
$(1BO_3+2BO_4)+(2BO_3+1BO_4)$	Layer[c] $[B^{III}B^{IV}_2O_4(OH)_2\cdot B^{III}_2B^{IV}O_3(OH)_3]^{nn-}_{nn}$	$Mg[B_6O_7(OH)_5]_{2nn}{=}MgO\cdot 6B_2O_3\cdot 5H_2O$	[69]	(XXV)
$(2BO_3 + 2BO_4)$[d] $+ 1BO_3 + (1BO_3 + 2BO_4)$	Network $[B^{III}_2B^{IV}_2O_7\cdot B^{III}O_{1,5}B^{III}B^{IV}_2O_{4,5}\times$ $\times(OH)_2]^{4nnn-}_{nnn}$	$Ca_2[B_8O_{13}(OH)_2]_{nnn}{=}CaO\cdot 2B_2O_3\cdot 0{,}5H_2O$	[33]	(XXVI)
$(3BO_3+2BO_4)+(3BO_3+2BO_4)$	Layer $[B^{III}_3B^{IV}_2O_8(OH)\cdot B^{III}_3B^{IV}_2O_8(OH)]^{4nn-}_{nn}$	Biringuchite $Na_4[B_{10}O_{16}(OH)_2]_{nn}\cdot 2H_2O{=}2Na_2O\cdot 5B_2O_3\cdot 3H_2O$	[70]	(XXVII)
$(2BO_3+3BO_4)+1BO_3$	Cyclochain $[B^{III}_2B^{IV}_3O_{7,5}(OH)_3\times$ $\times B^{III}O_{0,5}(OH)_2]^{3n-}_n$	Caliborite $HKMg_2[B_6O_8(OH)_5]_{2n}\cdot 4H_2O{=}K_2O\cdot 4MgO\cdot 12B_2O_3\cdot 19H_2O$	[71]	(XXVIII)
$(3BO_3+3BO_4)+2BO_3$	Layer $[B^{III}_3B^{IV}_3O_{9,5}(OH)\cdot B^{III}_2O_{1,5}(OH)_3]^{2nn-}_{nn}$	Strontioborite $Sr[B_8O_{11}(OH)_4]_{nn}{=}SrO\cdot 4B_2O_3\cdot 2H_2O$ $Ca[B_8O_{11}(OH)_4]_{nn}{=}CaO\cdot 4B_2O_3\cdot 2H_2O$	[72] [73]	(XXIX) (XXX)
$(3BO_3+3BO_4)+(3BO_3+3BO_4)+2BO_3$	Layer $[B^{III}_3B^{IV}_3O_9(OH)_2\cdot B^{III}_3B^{IV}_3O_{9,5}(OH)\times$ $\times B^{III}_2O_{1,5}(OH)_3]^{4nn-}_{nn}$	Strontioginorite $(Sr, Ca)_2[B_{14}O_{20}(OH)_6]_{nn}\cdot 5H_2O=$ $=2(Sr, Ca)O\cdot 7B_2O_3\cdot 8H_2O$	[74]	(XXXI)
$(3BO_3+4BO_4)+1BO_3$	Cyclochain[e] $[B^{III}_3B^{IV}_4O_{11}(OH)_3\cdot B^{III}O(OH)]^{4n-}_n$	$Tl_4[B_8O_{12}(OH)_4]_n\cdot H_2O{=}Tl_2O\cdot 2B_2O_3\cdot 2H_2O$	[68, 32]	(XXXII)
$(4BO_3+5BO_4)+1BO_4+1BO_4$	Layer $\{B^{III}_4B^{IV}_5O_{14}(OH)_4\cdot[B^{IV}O(OH)_2]_2\}^{7nn-}_{nn}$	Preobrazhenskite $HMg_3[B_{11}O_{16}(OH)_8]_{nn}{=}6MgO\cdot 11B_2O_3\cdot 9H_2O$	[75]	(XXXIII)

[a] In order to maintain a unified treatment, on passing to the CRU of the anhydrous borates (see Section III), the subunits in the CRU and the CRU in the macroanions are distinguished in Fig.2 with respect to the connecting oxygen atoms[35] and not the boron–oxygen bonds.[25,34] For this reason, whereas the formulae of the CRU are identical, those of the subunits differ somewhat from those adopted in the literature.[25,34]

[b] The initial preoligomer is illustrated in Fig.1 (*D, b*); the formation of the polyanion is illustrated schematically in Fig.6.

[c] A characteristic feature of the phylloanion of this borate is the grafting of side branches ($2BO_3$ + $1BO_4$) to the main chain of the hydroboracite type—see (III) and (IV) in Table 1, as well as the cross-linking of these chains into layers via B–OH–B bridges[69] and not B–O–B bridges as is usually the case. Since two oxygen atoms (at the sites corresponding to grafting and cross-linking) are tricoordinate (with 2B and 1 H), the charge of the CRU does not agree with the number of B^{IV} atoms in it and is in fact equal to only −1 and not −3 [cf.also with (XX)–(XXII) in Table 1 and (XXIX)–(XXXI) in the present Table].

[d] The initial preoligomer is illustrated in Fig.1 (*D, a*).

[e] The CRU of the polyanion of the given borate can be regarded also as the dimer of the CRU of compound (XXIV) in the present Table.

and $Mg_2\{[B_4O_7]_{nnn}\}_2$, (XLIX) in Table 3,[101] and preobrazhenskite, (XXXIII) in Table 2, is converted into a mixture of $Mg_2\{[B_4O_7]_{nnn}\}_2$ and $Mg_2B_2O_5$ with a dimeric anion (on further heating, the former melts incongruently decomposing into the same compound $Mg_2B_2O_5$ and B_2O_5, which are in fact the final products of the thermal transformation of preobrazhenskite[103]). In the polymer chemistry of phosphates, this type of opening and transformation of the rings is attributed to heterolytic cleavage and the formation of zwitter-ions, the polymerisation proceeding subsequently in accordance with an ionic mechanism (Ref.5, p.91). As regards borates, it is known only (in relation to the so called calcium "octaborates". which are in fact tetraborates[108]), that although neither they themselves nor their dehydration products are electrically conducting, nevertheless electrical conductivity appears at the temperature of the BR [109] despite the fact that T_m is higher by 100 °C. However, electrical conductivity can be manifested also on homolytic cleavage of the rings accompanied by the appearance of radicals. EPR studies on the BR as well as its initiation by different methods might throw light on this question. Hitherto BR has been initiated mainly thermally, although in the chemistry of macromolecular compounds the radiation, mechanochemical, and other methods are used for the initiation of solid-phase polymerisation.[105]¶

The examples presented demonstrate differences in the structures of hydrated and anhydrous borates even when these contain the same cations and show that it is useful to consider separately these genetically interrelated compounds.

¶ Phenomena analogous to the BR effect are not a unique feature of borates. They occur also in the thermal transformations of aluminosilicates, for example, kaolinite (which consists of alternating polysiloxane and polyaluminoxane phylloanions[4] and is a component of natural clays), into mullite and silicon dioxide.[110] The latter are ingredients in the compositions of ceramic materials whose polymer-colloidal nature and composition are complex.[6,111]

III. ANHYDROUS OXOBORATES

1. Crystalline Compounds

The main methods for the preparation of crystalline anhydrous oxoborates are the BR considered above (for amorphous powders), synthesis from solutions or melts under normal and increased pressures, and also heat treatment of vitreous borates below T_m. In the last case, the process resembles the BR as regards its chain character (induction period, autoacceleration) the physical properties (density and hardness) of the crystals obtained from the amorphous powders and vitreous systems being identical.[77]

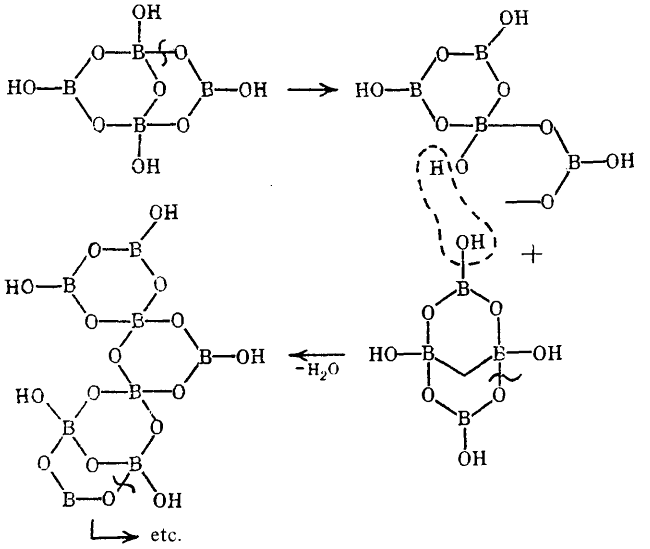

Figure 6. Schematic representation of the polymerisation reaction of borax to give kernite.[25]

The main principles governing the formation of the structures[26] are described below taking into account the postulates of the chemistry of macromolecular compounds.

1. The simplest groups in the structures are BO_3 and BO_4.
2. The monomeric and dimeric anions are made up only of BO_3 or only BO_4.
3. The simplest groups (subunits) can function as the CRU of the macroanions, which are usually formed as a result of the linking of the vertices of the BO_3 triangles and BO_4 tetrahedra via the p-bridges $>B{-}O{-}B<$, $>B{-}O{-}\overset{|}{\underset{|}{B}}{-}$, or $-\overset{|}{\underset{|}{B}}{-}O{-}\overset{|}{\underset{|}{B}}{-}$.†
4. Oligoanions with $n \geq 3$ can exist in the structures of anhydrous borates, but such oligoanions are more common as the CRU of the macroanions with a structure specific to anhydrous borates.
5. A decrease of M_xO_y/B_2O_3 (i.e. an increase of the modulus m) and an increase of the size of the metal cations (to a lesser extent) lead to an increase of the degree of polymerisation and of the density of the cross-linking of the macroanions (and also of the ratio BO_3/BO_4 for $M_xO_y/B_2O_3 \leq 1$), while an increase of the charge of the cations M^{y-} induces the opposite tendency.
6. Each O atom is usually linked to two B atoms (the ratio $BO_3/BO_4 = m-1$ is valid for such compounds having the composition $nM_xO_y.mB_2O_3$ when $m > 1$), but terminal (non-bridging) oxygen ions and transitional (bridging) oxygen atoms with hybrid coordinations with respect to boron of 3 and even 4 can be encountered.#
7. The phyllo- and tekto-anions of the anhydrous M^+ and M^{2+} borates exhibit a tendency towards twinning, frequently with formation of interpenetrating polymer networks (IPN).

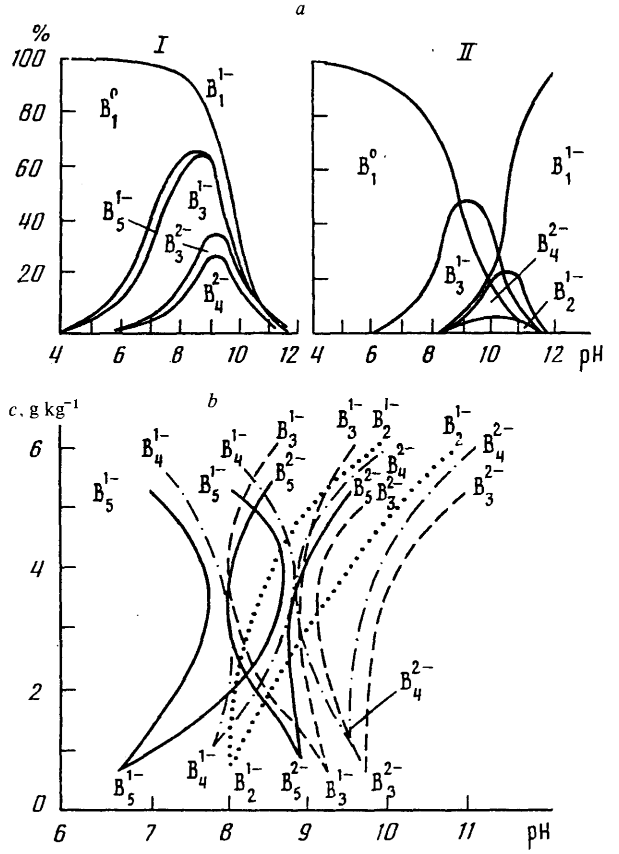

Figure 7. Borate homologues in aqueous solutions (B_n^{m-} is an abbreviated designation of the corresponding borates presented in Fig. 1): a) the fraction of the corresponding borate as a function of the pH of the solution at a boron concentration c = 0.4 M and T = 298 K (I) and also at c = 0.6 M and T = 393 K; the regions where they predominate as a function of the pH and the boron concentration c in the range 1–6 g kg^{-1} according to the data of Farmer[34] and Ozol[82]).

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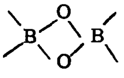
†An instance of the polymerisation of the BO_4 tetrahedra via  bridges is known—see (XCIX) in Table 4 and the corresponding remark in the same Table.

#See Figs. 9–12.

Fig. 8 presents the known varieties of the mono-, di-, and oligo-anions in the fully ionised (cationic) form. Specific examples of such borates are not considered here, as for hydrated borates in Section II. We shall only note that the pentaborate (Fig. 8, *D*), which is not mentioned in the monograph of Leonyuk and Leonyuk,[26] has been discovered in the structure $Bi_3O[B_5O_{11}] = 3Bi_2O_3.5B_2O_3$,[112] while the oligomer (Fig. 8, *E*) has been found in the structure $Pb_6.[B_{10}O_{21}] = 6PbO.5B_2O_3$.[113] The latter is not in fact a decaborate and consists of a modified (combined) oligoanion (two tetraborates grafted to one another via two BO_3 triangles).

Fig. 9 presents examples of the "usual" CRU in the macroanions of anhydrous crystalline borates and Table 3 lists the corresponding specific compounds.

Fig. 10 presents modified (combined) CRU and Table 4 the corresponding borates.

The fragments of the macroanions of certain borates quoted in Tables 3 and 4 are illustrated in Figs. 11 and 12. Fig. 13 demonstrates the formation of IPN.

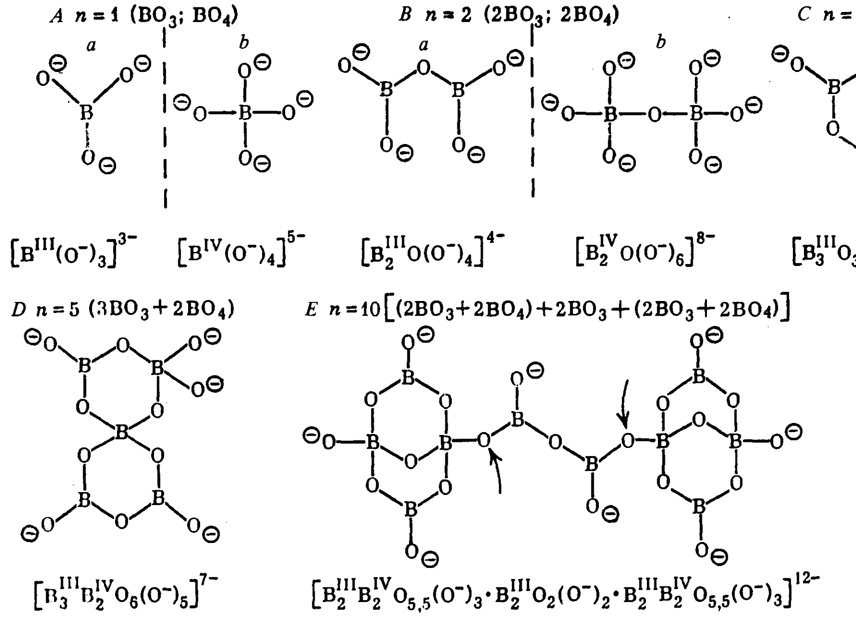


Figure 8. The monoanions, dianions, and oligoanions of anhydrous crystalline borates in the fully ionised (cationic) form.

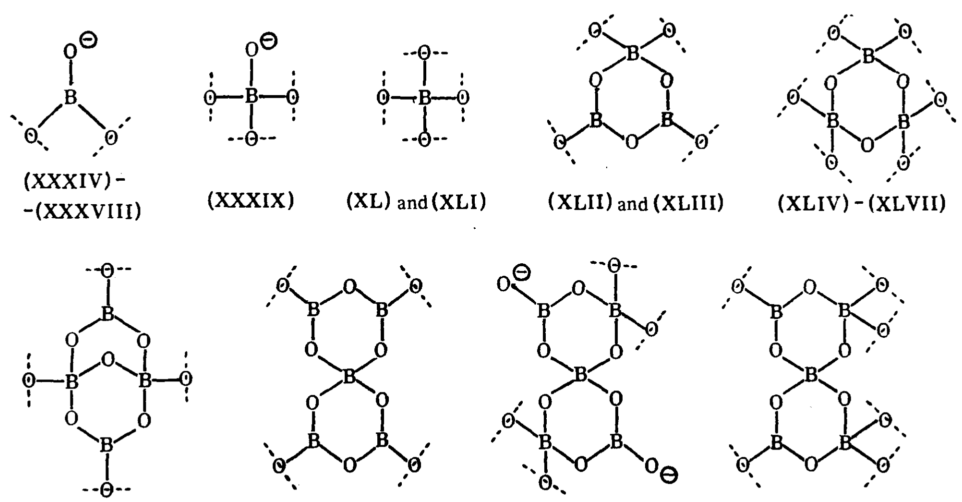


Figure 9. Examples of the "usual" CRU in the macroanions of anhydrous crystalline borates (the Roman numerals correspond to those adopted in Table 3 for specific compounds).

From the standpoint of the chemistry of macromolecular compounds, it is evident that, when the individual BO_3 (or BO_4) groups are linked predominantly by covalent bonds to other elementoxane groups (SiO_4, PO_4, AlO_4, etc.), forming the corresponding macroanions with the linkages B–O–E (for example, in the chain polyanions of calcium[175] or strontium[176] aluminoborates), then they are no longer isolated[26] and enter, in the form of subunits of a new kind, into the composition of the corresponding CRU in inorganic polyborelementoxanes, which are not considered here. Conversely, compounds of the type $La_2O_3.B_2O_3.2MoO_3$ and $La_2O_3.B_2O_3.2WO_3$ [compounds (XXXVII) and (XXXVIII) in Table 3], in the structure of which discrete MoO_4 and WO_4 tetrahedra are not in contact either with one another or with the chain polyboroxane polyanion, are not copolymers (inorganic polyboroelementoxanes) from the standpoint of the chemistry of macromolecular compounds, i.e. are not boromolybdates and borotungstates,[26] since the polyanions contain only B–O–B linkages. These compounds should be regarded rather as mixtures of a polyborate with a monomolybdate or

Table 3. Examples of polymeric anhydrous crystalline borates with the "usual" CRU (see also Figs. 9 and 11).

CRU[a] of macro-anions	Initial monomer or preoligomer	Form and formula of macroanion	Examples of specific compounds	Refs.	Designation
Monoborate	BO_3	Chain $[B^{III}O(O^-)]_n^{n-}$	$Li[BO_2]_n=\alpha\text{-}Li_2O\cdot B_2O_3$	[114]	(XXXIV)
			$Ca[(BO_2)_2]_n=CaO\cdot B_2O_3$—I	[115]	(XXXV)
			$Eu[(BO_2)_2]_n=EuO\cdot B_2O_3$	[116]	(XXXVI)
			$La_2[(BO_2)_2]_n\cdot[MoO_4]_2=La_2O_3\cdot B_2O_3\cdot 2MoO_3$	[117]	(XXXVII)
			$La_2[(BO_2)_2]_n\cdot[WO_4]_2=La_2O_3\cdot B_2O_3\cdot 2WO_3$	[117]	(XXXVIII)
	BO_4	Layer[b] $[B^{IV}O_{1.5}(O^-)]_{nn}^{2nn-}$	$NdAl_2O_{0.5}[(BO_{2.5})_4]_{nn}=Nd_2O_3\cdot 2Al_2O_3\cdot 4B_2O_3$	[118]	(XXXIX)
			$Li[BO_2]_{nnn}=\gamma\text{-}Li_2O\cdot B_2O_3$	[119]	(XL)
		Network $[B^{IV}O_2]_{nnn}^{nnn-}$	$Zn_4O[(BO_2)_6]_{nnn}=4ZnO\cdot 3B_2O_3{}^{c}$	[120]	(XLI)
Triborate	$2BO_3^{\circ}+1BO_4$	Network $[B_2^{III}B^{IV}O_5]_{nnn}^{nnn-}$	$Cs[B_3O_5]_{nnn}=Cs_2O\cdot 3B_2O_3$	[121]	(XLII)
	$3BO_4$	Network[d] $[B_3^{IV}O_6]_{nnn}^{3nnn-}$	$Li[B_3O_5]_{nnn}=Li_2O\cdot 3B_2O_3$	[122]	(XLIII)
			$Ca_3[(B_3O_6)_2]_{nnn}=CaO\cdot B_2O_3$—IV	[123]	(XLIV)
			$Sr_3[(B_3O_6)_2]_{nnn}=SrO\cdot B_2O_3$—IV	[124]	(XLV)
			$Cu_3[(B_3O_6)_2]_{nnn}=CuO\cdot B_2O_3$	[125]	(XLVI)
			$Pd_3[(B_3O_6)_2]_{nnn}=PdO\cdot B_2O_3$	[126]	(XLVII)
Tetraborate[e]	$2BO_3+2BO_4$	Network (two IPN)[f] $\{[B_2^{III}B_2^{IV}O_7]_{nnn}^{2nnn-}\}_2$	$Li_4\{[B_4O_7]_{nnn}\}_2=Li_2O\cdot 2B_2O_3$	[127]	(XLVIII)
			$Mg_2\{[B_4O_7]_{nnn}\}_2=MgO\cdot 2B_2O_3$	[128]	(XLIX)
			$Mn_2\{[B_4O_7]_{nnn}\}_2=MnO\cdot 2B_2O_3$	[129]	(L)
			$Zn_2\{[B_4O_7]_{nnn}\}_2=ZnO\cdot 2B_2O_3$	[130]	(LI)
			$Cd_2\{[B_4O_7]_{nnn}\}_2=CdO\cdot 2B_2O_3$	[131]	(LII)
			$Fe_2\{[B_4O_7]_{nnn}\}_2=FeO\cdot 2B_2O_3$	[132]	(LIII)
Pentaborate	$4BO_3+1BO_4$	Network (two IPN)[g] $\{[B_4^{III}B^{IV}O_8]_{nnn}^{nnn-}\}_2$	$K_2\{[B_5O_8]_{nnn}\}_2=\alpha\text{-}K_2O\cdot 5B_2O_3$	[133]	(LIV)
			$K_2\{[B_5O_8]_{nnn}\}_2=\beta\text{-}K_2O\cdot 5B_2O_3$	[134]	(LV)
			$LaCo[B_5O_{10}]_{nn}=La_2O_3\cdot 2CoO\cdot 5B_2O_3$	[135]	(LVI)
	$2BO_3+3BO_4$		$NdCo[B_5O_{10}]_{nn}=Nd_2O_3\cdot 2CoO\cdot 5B_2O_3$	[136]	(LVII)
		Layer $[B_2^{III}B_3^{IV}O_8(O^-)_2]_{nn}^{5nn-}$	$SmCo[B_5O_{10}]_{nn}=Sm_2O_3\cdot 2CoO\cdot 5B_2O_3$	[137]	(LVIII)
			$HoCo[B_5O_{10}]_{nn}=Ho_2O_3\cdot 2CoO\cdot 5B_2O_3$	[138]	(LIX)
			$YCo[B_5O_{10}]_{nn}=Y_2O_3\cdot 2CoO\cdot 5B_2O_3$	[139]	(LX)
			$LaMg[B_5O_{10}]_{nn}=La_2O_3\cdot 2MgO\cdot 5B_2O_3$	[140]	(LXI)
		Layer $[B_2^{III}B_3^{IV}O_9]_{nnn}^{3nnn-}$	$Eu_2[B_5O_9]_{nnn}\cdot Cl=3EuO\cdot EuCl_2\cdot 5B_2O_3$	[141]	(LXII)
			$Eu_2[B_5O_9]_{nnn}\cdot Br=3EuO\cdot EuBr_2\cdot 5B_2O_3$	[141]	(LXIII)

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[a] The CRU of the macroanions[27] may not be identical with the stereorepeating units; for example, the stereorepeating units in compounds (XXXIV)–(XXXVIII) are made up of two BO_3 triangles.

[b] When the tetrahedra are joined together into chains, the stereorepeating unit is $2BO_4$, when the chains are joined up to form a layer, rings consisting of six BO_4 are produced, and when the layers alternate, the $\gt B-O^-$ terminal bonds in the layers are alternately directed to one side or another of the layer, so that overall a structure similar to micas is formed.[4]

[c] The tetrahedra in the tektoanion of this borate are linked in such a way that a "Chinese lantern" with six "windows" (rings made up of $4BO_4$) and eight "windows" (rings made up of $6BO_4$) is produced.

[d] Although the borates (XLIV) and (XLV) have identical CRU, they differ from compounds (XLVI) and (XLVIII) in the way that the CRU are joined together in space.

[e] As in Section II, the "kernite-like" CRU have been classified as modified units—see compounds (LXX) and (LXXI) in Table 4.

[f] Although the borate (XLVIII) has the same CRU, it differs from compounds (XLIX)–(LIII) in the stereorepeating units.

[g] The borates (LIV) and (LV) differ in the disposition of the CRU relative to the double rotational axes (in one case the axes pass near the ends of the pentaborate groups and in the other they pass virtually through their centres).

tungstate just as compounds (XII) and (XIII) in Table 1 are mixtures of phylloborates with monoborate.

It is seen from the data presented that the macroanions of anhydrous crystalline borates are more complex and varied than the hydrated macroanions (see also, Section IV). Modified CRU, distinguished by a great variety, are encountered among them more frequently. The macroanions themselves have a three-dimensional structure and more rarely two- and mono-dimensional structures. Network macroanions then tend to form IPN. All these factors prevent a stereoregular packing of the macroanions, greatly hindering the formation of polymeric single crystals of anhydrous borates. This requires the maintenance of a series of special conditions, including prolonged isothermal treatment, the introduction of seeds, etc.[26] When polymeric borate melts are cooled in the usual way, they pass to a vitreous state.

2. Vitreous Oxoborates

Many borates, including the borates of all the Group IA and IIA elements, zinc and cadmium (Group IIB), thallium (Group IIIA), lanthanum (IIIB), lead (Group IVA), and bismuth (Group VA),[7] tellurium (Group VIA),[177] and other elements, let alone binary and more complex borates, have been obtained in a vitreous state. In contrast to the crystalline borates, the vitreous borates are non-equilibrium systems, i.e. in any specific borate glass one of the many structures characteristic of melts having the same composition is fixed.

Table 5 makes it possible to compare the boundaries of the glass formation regions in certain borate systems[177,178] with data concerning the crystalline compounds existing in these regions.[179] It is easily seen that all the compounds with known structures are in this instance the polymers listed

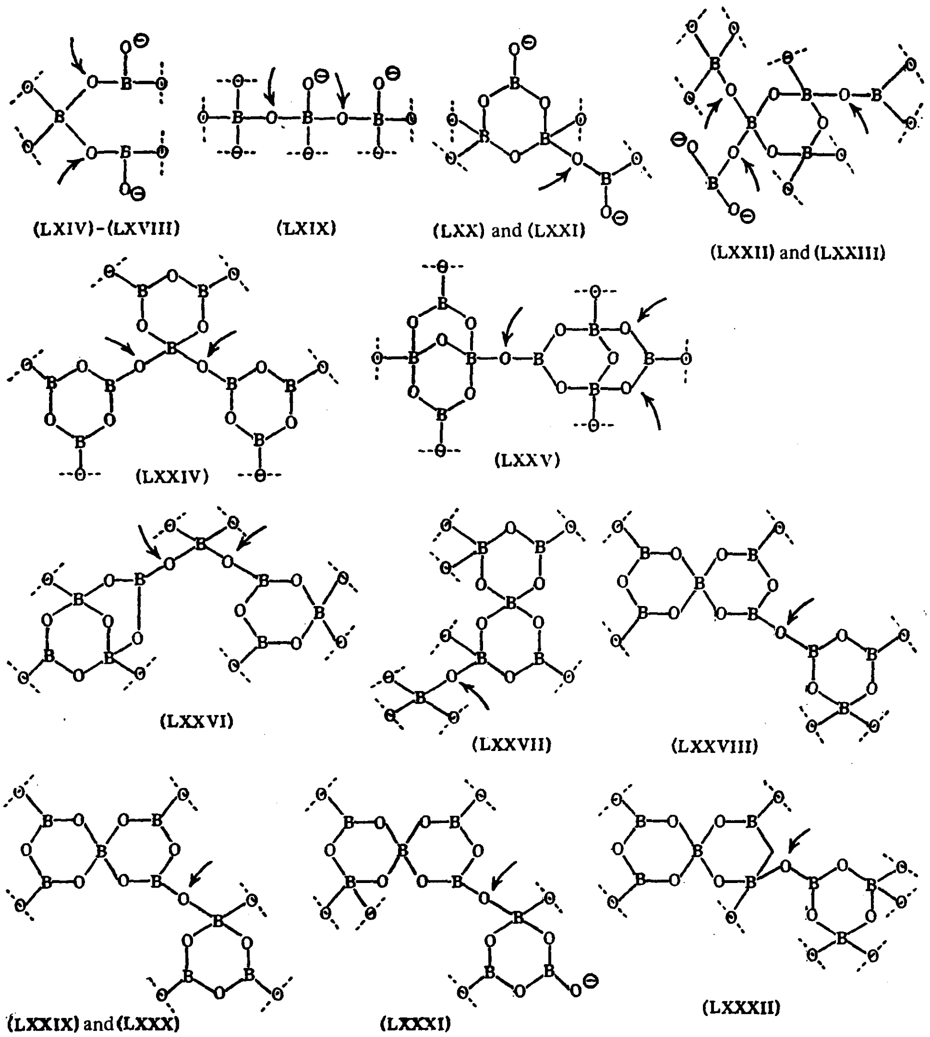

Figure 10. Examples of modified (combined) CRU in the macroanions of anhydrous crystalline borates in Table 4 (the notation is analogous to that adopted in Figs. 2 and 9); for the CRU of the macroanions (XCVI)–(XCVIII), the numerals opposite the connecting oxygen atoms sp^2-hybridised with respect to boron represent the fraction of such atoms contributed by neighbouring CRU.

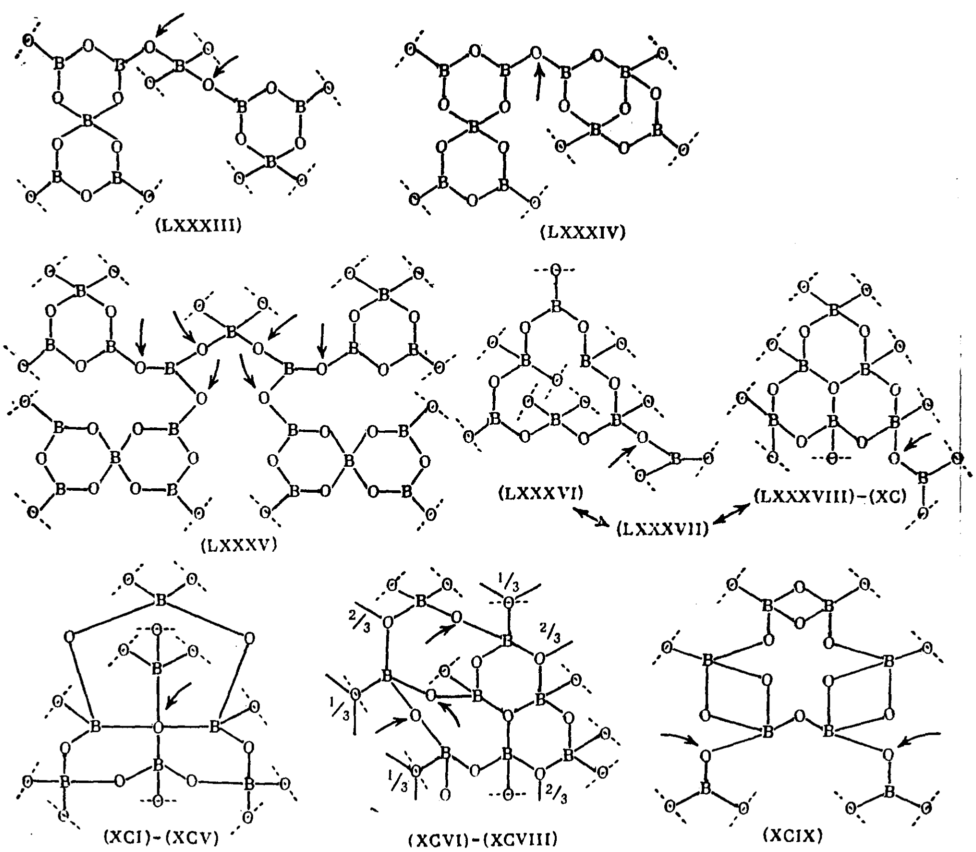

Figure 10 (contd.).

in Tables 3 and 4. This suggests that the structures which have not so far been elucidated also have a polymeric structure (or at least an oligomeric structure with $n \geq 5$).

The glass formation regions are usually bounded by compositions forming optically homogeneous glasses (these boundaries depend on the experimental conditions—the volume of the melt and the rate of its cooling). Polymeric borates can also form optically inhomogeneous glasses. In one case these are liquating glasses,[181,182] the appearance of which is a consequence of the immiscibility, with phase inversion, characteristic of colloidal polymer systems.[183] In another these are partly crystallising glasses, whose formation may be caused by the crystallisation of chain polyanions with a simple configuration or by the formation of rigid networks of the type of boracites. In the latter case, the fraction of flexible B–O–B bonds diminishes as the transitional O atoms undergo a change from a state involving sp-hybridisation to states involving sp^2- and sp^3-hybridisation with B atoms (the –O– bridges are replaced by $\overset{|}{\underset{/\ \backslash}{O}}$ and even $-\overset{|}{\underset{|}{O}}-$), i.e. the configurational-conformational statistics of the polymers is impoverished. However, the low-molecular-weight anionic fraction, especially monomeric borates, crystallises most readily, even under conditions where the melts are subjected to intense cooling. In other words, the tendency of a particular substance towards glass formation is determined not only and not so much by kinetic as by structural factors.[184] Among them, the leading role is due to the presence in the structure of atoms or groups of atoms connected by directional bonds[184]§ and such structures should possess fairly pronounced flexibility, ensuring a definite set of conformations and configurations (see Section IV).

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§The latter agrees with all the criteria of the polymeric structure of matter.[1,185]

The fact that glasses are formed in boron oxide–zinc oxide (cadmium, lead, and bismuth oxide) systems when the B_2O_3 content is less than 50 mole % suggests that the above elements are incorporated into the macroanionic network of the glass with formation of B–O–E linkages.[7] In particular, this has been confirmed for the $PbO–B_2O_3$ system by NMR data[7] and for the $ZnO–B_2O_3$ system by the results of the EPR study of the mechanodegradation of the corresponding

Table 4. Examples of polymeric anhydrous crystalline borates with modified (combined) CRU (see also Figs. 10 and 12).

Grafted groups (CRU subunits)	Form and formula of macroanion	Examples of specific compounds (the trivial names of the natural borates are also given)	Refs.	Designation
$1BO_3+1BO_4+1BO_3$	Cyclochain[a] $[B^{III}O(O^-)\cdot B^{IV}O_2\cdot B^{III}O(O^-)]_n^{3n-}$ Layer[b] $[B^{III}O(O^-)\cdot B^{IV}O_2\cdot B^{III}O(O^-)]_{nn}^{3nn-}$	$La[B_3O_6]_n{=}La_2O_3\cdot 3B_2O_3$ $Nd[B_3O_6]_n{=}Nd_2O_3\cdot 3B_2O_3$ $Sm[B_3O_6]_n{=}Sm_2O_3\cdot 3B_2O_3$ $Gd[B_3O_6]_n{=}Gd_2O_3\cdot 3B_2O_3$ $Bi[B_3O_6]_{nn}{=}Bi_2O_3\cdot 3B_2O_3$	[142] [143] [144] [144] [145]	(LXIV) (LXV) (LXVI) (LXVII) (LXVIII)
$1BO_4+1BO_4+1BO_4$	Layer[c] $[B^{IV}O_2\cdot B^{IV}O_{1.5}(O^-)\cdot B^{IV}O_{1.5}(O^-)]_{nn}^{5nn-}$	Yohachidolite $CaAl[B_3O_7]_{nn}{=}2CaO\cdot Al_2O_3\cdot 3B_2O_3$	[146]	(LXIX)
$(1BO_3+2BO_4)+1BO_3{}^{r}$	Cyclochain $[B^{III}B_2^{IV}O_5(O^-)\cdot B^{III}O(O^-)]_n^{4n-}$	Calciborite $Ca_2[B_4O_8]_n{=}CaO\cdot B_2O_3$—II $Ag_4[B_4O_8]_n{=}Ag_2O\cdot B_2O_3$	[147] [148]	(LXX) (LXXI)
$3BO_4+1BO_4+1BO_3+1BO_3$	Network $[B_3^{IV}O_6\cdot B^{IV}O_2\cdot B^{III}O_{1.5}\cdot B^{III}O_{0.5}(O^-)_2]_{nnn}^{6nnn-}$	$Ca_3[B_6O_{12}]_{nnn}{=}CaO\cdot B_2O_3$—III $Sr_3[B_6O_{12}]_{nnn}{=}SrO\cdot B_2O_3$—III	[149] [124]	(LXXII) (LXXIII)
$3BO_3+(2BO_3+1BO_4)+3BO_3$	Network (two IPN) $\{[B_3^{III}O_{4.5}\cdot B_2^{III}B^{IV}O_5\cdot B_3^{III}O_{4.5}]_{nnn}^{nnn-}\}_2$	$Cs_2\{[B_9O_{14}]_{nnn}\}_2{=}\beta\text{-}Cs_2O\cdot 9B_2O_3$	[150]	(LXXIV)
$(2BO_3+2BO_4)+(1BO_3+2BO_4)+1BO_3$	Network $[B_2^{III}B_2^{IV}O_7\cdot B^{III}B_2^{IV}O_{5.5}\cdot B^{III}O_{1.5}]_{nnn}^{4nnn-}$	$K_4[B_8O_{14}]_{nnn}{=}K_2O\cdot 2B_2O_3$	[151]	(LXXV)
$(2BO_3+2BO_4)+1BO_4+(2BO_3+1BO_4)$	Network $[B_2^{III}B_2^{IV}O_7\cdot B^{IV}O_2\cdot B_2^{III}B^{IV}O_5]_{nnn}^{4nnn-}$	$Ca_2[B_8O_{14}]_{nnn}{=}CaO\cdot 2B_2O_3$—II	[152]	(LXXVI)
$(2BO_3+3BO_4)+1BO_4$	Network $[B_2^{III}B_3^{IV}O_9\cdot B^{IV}O_2]_{nnn}^{4nnn-}$	$Ca_2[B_6O_{11}]_{nnn}{=}2CaO\cdot 3B_2O_3$	[153]	(LXXVII)
$(4BO_3+1BO_4)+(2BO_3+1BO_4)$	Network (two IPN)[e] $\{[B_4^{III}B^{IV}O_8\cdot B_2^{III}B^{IV}O_5]_{nnn}^{2nnn-}\}_2$	$Na_4\{[B_8O_{13}]_{nnn}\}_2{=}\alpha\text{-}Na_2O\cdot 4B_2O_3$ $Ag_{2.4}Na_{1.6}\{[B_8O_{13}]_{nnn}\}_2{=}0{,}6\,Ag_2O\cdot 0{,}4\,Na_2O\cdot 4B_2O_3$ $Ba_2\{[B_8O_{13}]_{nnn}\}_2{=}BaO\cdot 4B_2O_3$	[154] [155] [156]	(LXXVIII) (LXXIX) (LXXX)
$(3BO_3+2BO_4)+(2BO_3+1BO_4)$	Layer $[B_3^{III}B_2^{IV}O_{8.5}\cdot B_2^{III}B^{IV}O_{4.5}\times$ $\times(O^-)]_{nn}^{4nn-}$	$Na_4[B_8O_{14}]_{nn}{=}\alpha\text{-}Na_2O\cdot 2B_2O_3$	[157]	(LXXXI)
$(3BO_3+2BO_4)+(1BO_3+2BO_4)$	Network $[B_3^{III}B_2^{IV}O_{8.5}\cdot B^{III}B_2^{IV}O_{5.5}]_{nnn}^{4nnn}$	$Ba_2[B_8O_{14}]_{nnn}{=}BaO\cdot 2B_2O_3$	[158]	(LXXXII)
$(4BO_3+1BO_4)+1BO_4(2BO_3+1BO_4)$	Layer (2 layers)[f] $\{[B_4^{III}B^{IV}O_8\cdot B^{IV}O_2\cdot B_2^{III}B^{IV}O_5]_{nn}^{3nn-}\}_2$	$Na_6\{[B_9O_{15}]_{nn}\}_2{=}\beta\text{-}Na_2O\cdot 3B_2O_3$	[159]	(LXXXIII)
$(4BO_3+1BO_4)+(2BO_3+2BO_4)$	Network (two IPN)[g] $\{[B_4^{III}B^{IV}O_8\cdot B_2^{III}B_2^{IV}O_7]_{nnn}^{3nnn-}\}_2$	$Na_6\{[B_9O_{15}]_{nnn}\}_2{=}\alpha\text{-}Na_2O\cdot 3B_2O_3$	[160]	(LXXXIV)
$1BO_4+2\cdot[(4BO_3+1BO_4)+1BO_3+$ $+(2BO_3+1BO_4)]$	Network $[B^{IV}O_2\cdot 2(B_4^{III}B^{IV}O_8\cdot B^{III}O_{1.5}\times$ $\times B_2^{III}B^{IV}O_5)]_{nnn}^{5nnn-}$	$K_5[B_{19}O_{31}]_{nnn}{=}5K_2O\cdot 19B_2O_3$	[161]	(LXXXV)
$(3BO_3+3BO_4)+1BO_3$	Network[h] $[B_3^{III}B_3^{IV}O_{10.5}\cdot B^{III}O_{1.5}]_{nnn}^{3nnn-}$	$Li_4Cl[B_7O_{12}]_{nnn}{=}\gamma\text{-}3Li_2O\cdot 2LiCl\cdot 7B_2O_3$ $Li_5Cl[B_7O_{12.5}]_{nnn}{=}4Li_2O\cdot 2LiCl\cdot 7B_2O_3{}^{i}$	[162] [163]	(LXXXVI) (LXXXVII)

Table 4 (cont'd).

n: Grafted groups (CRU subunits)	Form and formula of macroanion	Examples of specific compounds (the trivial names of the natural borates are also given)	Refs.	Designation
$6BO_4+1BO_3$	Network $[B_6^{IV}O_{11.5}\cdot B^{III}O_{1.5}]_{nnn}^{5nnn-}$	α-Boracite $Mg_3Cl[B_7O_{13}]_{nnn}=\alpha\text{-}5MgO\cdot MgCl_2\cdot 7B_2O_3$ $Fe_{2.4}Mg_{0.6}Cl[B_7O_{13}]_{nnn}=5(Fe, Mg)O\cdot(Fe, Mg)Cl_2\cdot 7B_2O_3$ $Ni_3Br[B_7O_{13}]_{nnn}=5NiO\cdot NiBr_2\cdot 7B_2O_3$	[164] [164] [165]	(LXXXVIII) (LXXXIX) (XC)
$7BO_4$	Network $[B_7^{IV}O_{13}]_{nnn}^{5nnn-}$	β-Boracite $Mg_3Cl[B_7O_{13}]_{nnn}=\beta\text{-}5MgO\cdot MgCl_2\cdot 7B_2O_3$ $Mg_3Br[B_7O_{13}]_{nnn}=5MgO\cdot MgBr_2\cdot 7B_2O_3$ $Co_3I[B_7O_{13}]_{nnn}=5CoO\cdot CoI_2\cdot 7B_2O_3$ $Cu_3Br[B_7O_{13}]_{nnn}=5CuO\cdot CuBr_2\cdot 7B_2O_3$ $Cd_3S_{0.5}[B_7O_{13}]_{nnn}=5CdO\cdot CdS\cdot 7B_2O_3$	[166] [167] [168] [168] [169]	(XCI) (XCII) (XCIII) (XCIV) (XCV)
$6BO_4+2BO_4$	Network $[B_6^{IV}O_{10.5}\cdot B_2^{IV}O_{2.5}]_{nnn}^{4nnn-}$	$Eu_2[B_8O_{14}]_{nnn}=EuO\cdot 2B_2O_3$ $Sr_2[B_8O_{14}]_{nnn}=SrO\cdot 2B_2O_3$ $Pb_2[B_8O_{14}]_{nnn}=PbO\cdot 2B_2O_3$	[170] [171] [171]	(XCVI) (XCVII) (XCVIII)
$6BO_4+2BO_3$	Layer[i] $[B_6^{IV}O_{12}\cdot 2B^{III}O_{1.5}]_{nn}^{6nn-}$	$Na_2Zn_2MnB_{4.67}O_{11}=3Na_2O\cdot 6ZnO\cdot 3MnO\cdot 7B_2O_3^{k}$	[172]	(XCIX)

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[a] When two CRU are joined together, a modified tetraborate ring is formed in the chain—see Fig.12 (LXIV)–(LXVII).

[b] When the CRU are joined together, "windows" consisting of rings made up of ($4BO_3$ + $4BO_4$) are produced in the layer.

[c] When the CRU are joined together, two forms of "windows" consisting of rings made up of $4BO_4$ and $6BO_4$ are produced in the layer.

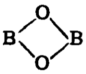
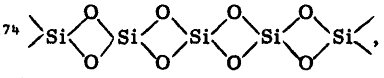
[d] "Kernite-like" CRU—see also (XXIII) and (XXIV) in Table 2.

[e] As can be seen from Fig.10, compound (LXXVIII) differs from compounds (LXXIX) and LXXX) by the different ways in which the triborate subunit is joined to the pentaborate subunit in the CRU.

[f] Two layers are cross-linked by oxygen bridges (between the pentaborate subunits of the CRU and the BO_4 tetrahedra).

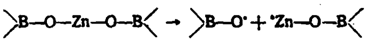
[g] Thus the metastable low-temperature β-form, having the same overall composition as the α-form, undergoes changes both in the steric structure of the macroanions and in the structure of the CRU subunits.

[h] The borate (LXXXVII) has a structure transitional between those of (LXXXVI) and (LXXXVIII). Whereas in compound (LXXXVI) the site of the 13th oxygen atom (at the centre of the ring) is unoccupied, in compound (LXXXVIII) it is fully occupied, while in compound (LXXXVII) it is partially occupied.

[i] If subsequent refinement confirms the interpretation of Bondareva et al.[172], it will be necessary to recognise the possibility of the anion polymerisation not only via B–O–B bridges but also via  bridges. In this connection one should note that the initial interpretation of the structure of the borate (XCVII) also assumed such a possibility,[173] but subsequently it was regarded as incorrect.[26,171] However, there is no fundamental prohibition of such polymerisation (see also Section IV). For example, the so called "fibrous" W-form of silicon dioxide, polymerising from the gas phase and having the chain structure[174] , i.e. the SiO_4 tetrahedra are in this case also joined together via their edges, is known in the chemistry of silicates. However, this product is unstable and after isothermal treatment is gradually transformed into the usual three-dimensional varieties of silicon dioxide (initially, at 473–1073 K, into tridymite and at higher temperatures into cristobalite), where the tetrahedra in the network are joined together in the usual way—via vertices (Si–O–Si) bridges—although different CRU are in fact produced.

[j] Boron is not present solely as part of the composition of the purely borate macroanion and part of it participates in the form of BO_3 triangles together with the ZnO_4 tetrahedra in the construction of the "cationic" part of the structure.[172]

glasses.[186] In the latter case the mechanodegradation of the macroanions involves precisely the B–O–Zn linkages, which are weaker¶ than the B–O–B linkages:[186]



As already mentioned, consideration of such copolymers is outside the framework of this review. The above results[186] have attracted attention primarily because of the very fact of the detection of radicals in the mechanical breakdown of borate glasses, since in low-molecular-weight compounds the dissociation of chemical bonds with formation of radicals does not occur under such an influence,[84] i.e. the phenomenon of mechanodegradation is characteristic of polymers alone.[84] Together with polymer-analogue transformations, the

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¶ In the terminology of the chemistry of glass,[187] zinc behaves in this instance as a modifier-intermediate.

exchange interaction of the macromolecules, etc. it is a specific chemical property of macromolecular compounds. The macromolecular nature of the substance is also manifested in a series of specific physical properties. These include the capacity for fibre and film formation, adhesion (binding) properties, orientation effects in electric, magnetic, and mechanical fields (in the last case up to crystallisation on stretching), and the ability to pass to the highly elastic state (non-Newtonian flow of melts and solutions, dissolution with preliminary swelling, immiscibility in the plastic state, characteristic features of the change in heat capacity at a low temperature, the presence of a spectrum of relaxation times, etc.$^{188-190}$ A number of similar properties have also been shown by vitreous borates.$^{1,7,184,191-193}$ The effect associated with the orientation of the structure of the sodium borate glass on vitrification in weak (0.07 and 0.8 T) magnetic fields may serve as one of the new examples of this kind.^{194} Similar effects have been observed for organic polymers and diamagnetic liquid crystals and, when the number of elementary units in molecules of such substances is of the order of 10^6–10^8, orientation is already achieved at a magnetic induction $B \approx 0.1$ T.^{194}

Overall, the concept of the presence in the structure of a covalently bound element–oxygen "network" is nowadays virtually generally accepted for borate (and other oxides) glasses,$^{1,7,35,184,187,191-193}$ etc. In this case the term "network" includes the concept of macroionic element–oxygen chains or segments of these chains (including highly branched chains), two-dimensional layers, and also intrinsically three-dimensional networks and their fragments. Although the discussion concerning the structure of the last features is still continuing,^{195,196} as regards vitreous borates,^{35} there are numerous experimental data demonstrating the presence in such a "network" of CRU analogous to those shown in Figs.9 and 10 together with the corresponding metal cation clusters. However, for thermodynamic and kinetic reasons, these CRU are frequently different for crystals and glasses of the same composition, for example,

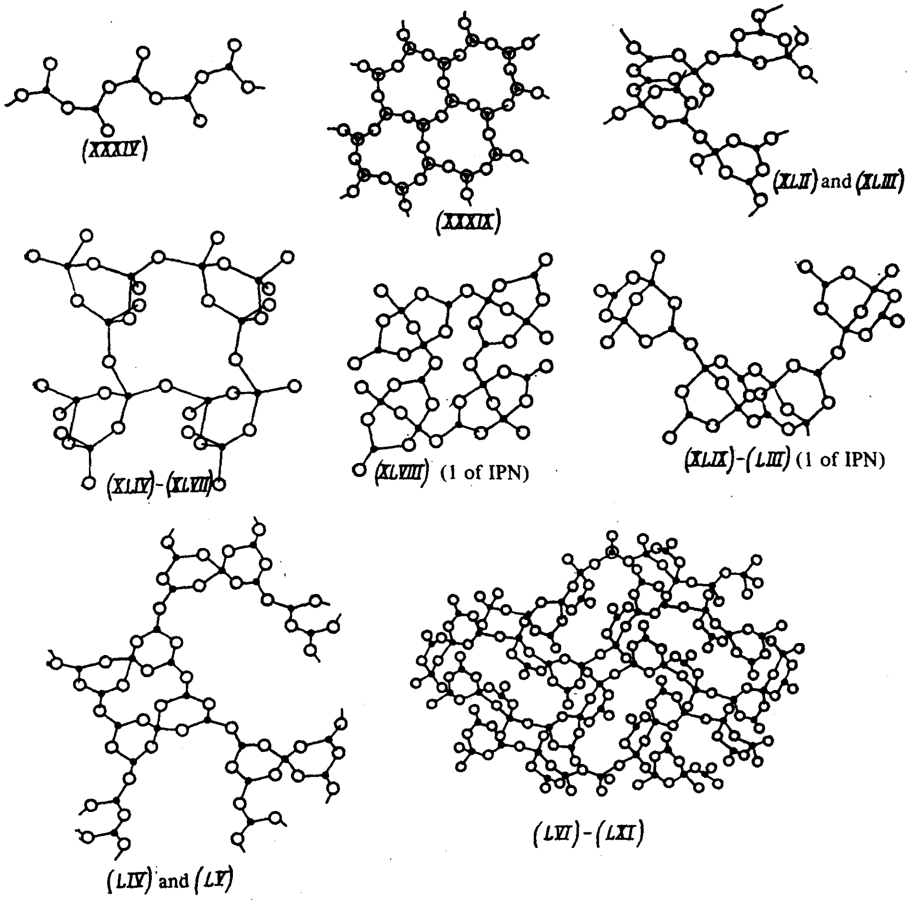

Figure 11. Fragments of the macroanions of certain borates in Table 3.

the $SrO.2B_2O_3$ CRU are not the same in the crystalline and vitreous states.[35] At the same time, the presence in the "network" of borate glasses of CRU analogous to (XXXIV) to (XXXVIII), (XLII) and (XLIII), (XLVIII)–(LIII), and (LIV) and (LV) in Fig. 9 and (LXXVIII) and (LXXXI) in Fig. 10, as well as the CRU subunits (LXXIV) and (LXXV) in the same figure can now be regarded as established.[35] Evidently, BO_3 and BO_4 can also function as independent CRU of the network and its fragments. The idea of a covalently-bound macroionic network in vitreous borates would be incomplete if one disregarded the possibility of its further differentiation already at the polymer–colloidal level of structural organisation (see the next Section).[181–183]

In contrast to the abbreviations Δ and *T* (or *t*) adopted for BO_3 and BO_4 in the crystal chemistry of borates,[25,26] in the chemistry of vitreous borates[35] a more far-reaching

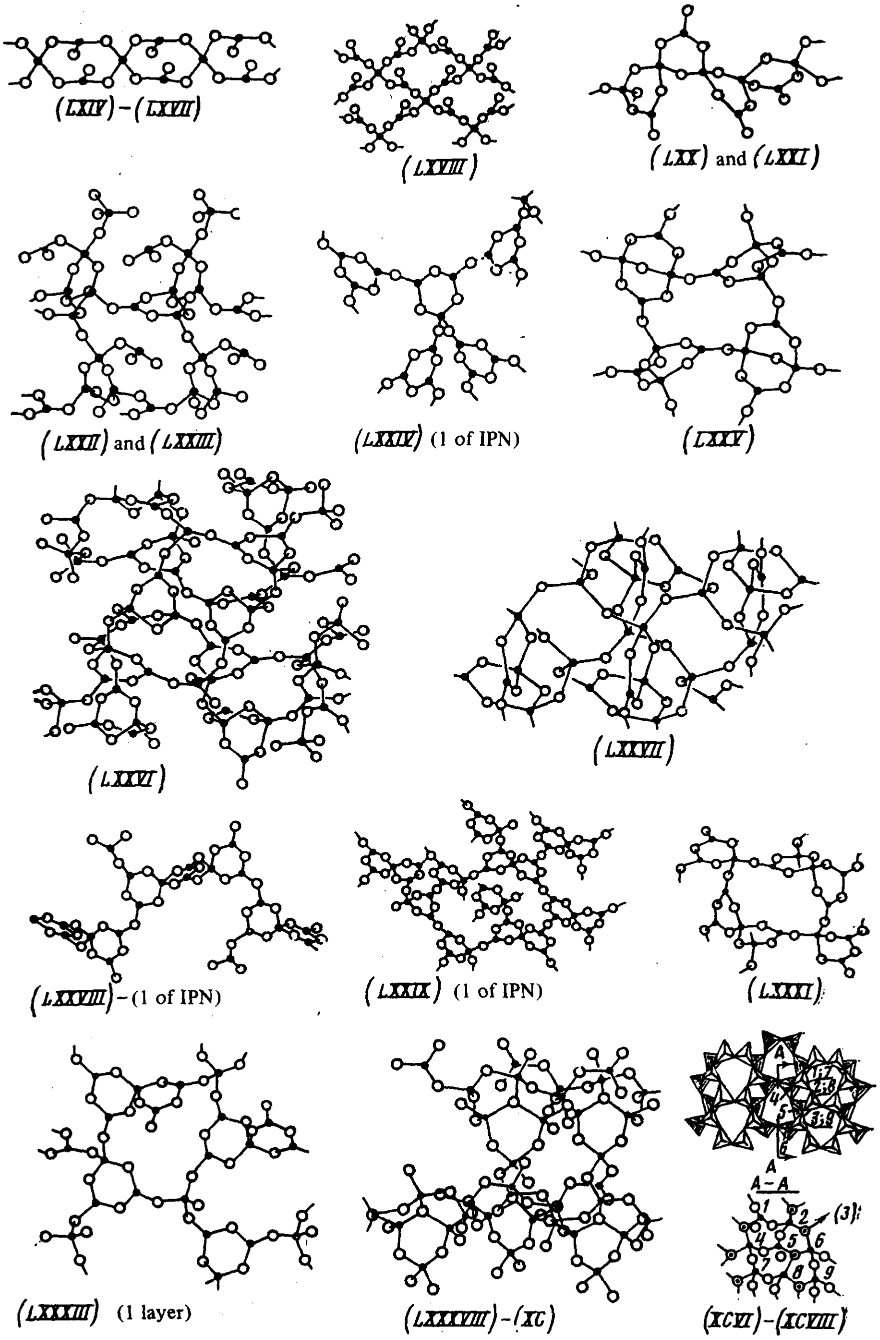

Figure 12. Fragments of the macroanions of certain borates in Table 4 [the A–A view for the clinographic (XCVI)–(XCVIII) projection—cf. with the planar representation of the corresponding CRU in Fig. 10].

gradation has been adopted in the abbreviations for borate groups together with a terminology based on chemical composition and not structure (Table 6). Here it is easy to put $BO_3 = a$, $BO'_3 = b$, $BO''_3 = b''$, $BO'''_3 = b'''$, $BO_4 = c$, etc. At the same time the term "diborate" for what is actually a tetraborate CRU and the term "tetraborate" for the modified CRU (LXXVIII) in Fig. 10 are unjustified. The use of double Greek prefixea to designate heterochain CRU with identical n ("di-triborate", "di-pentaborate") is also not entirely apt—it implies the dimerisation of the CRU.

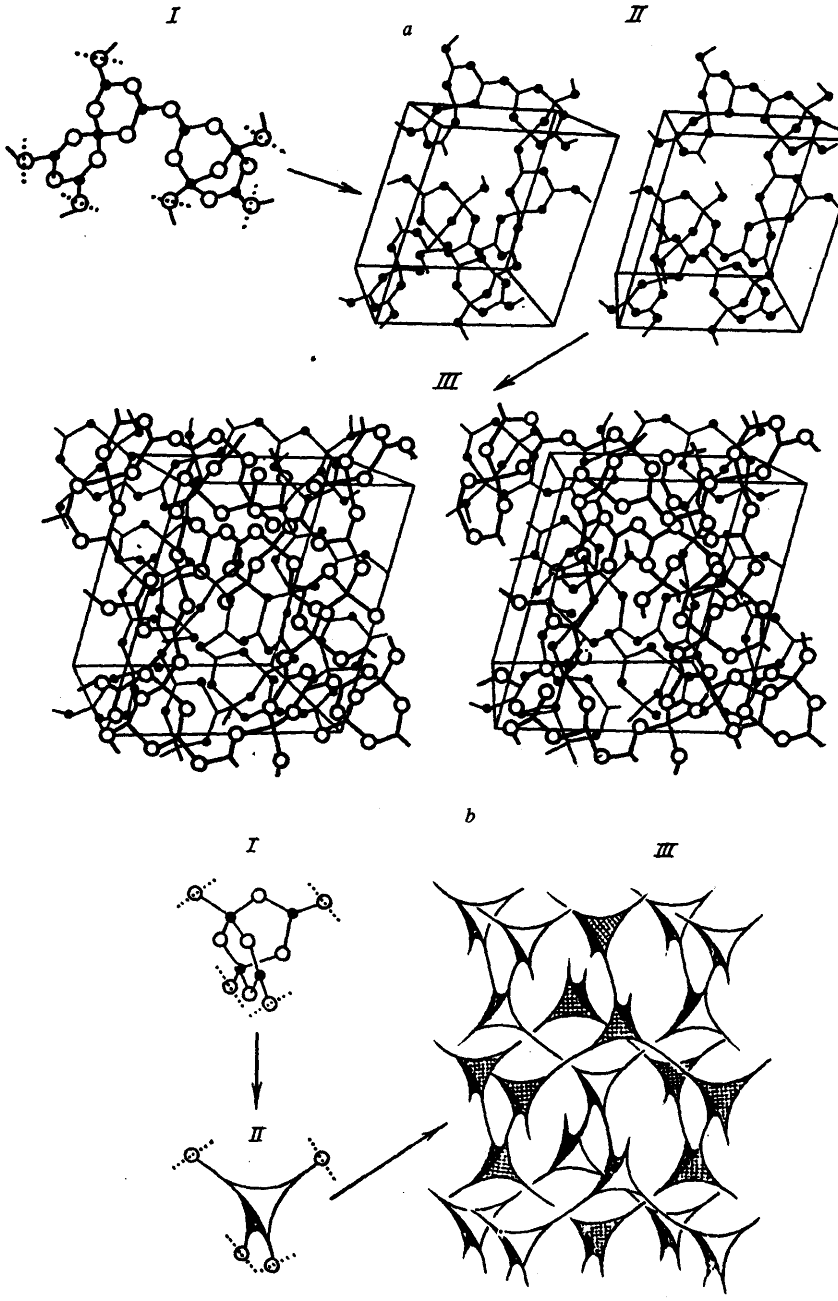

Figure 13. Examples of the formation of the IPN from the macroanions of anhydrous borates: *a*) for the borate (LXXXIV) in Table 4 [stereopairs based on "spherical" models were used: *I*) CRU; *II*) network made up of CRU *I*; *III*) IPN made up of two networks *II*]; *b*) for the borate (XLIX) in Table 3 [a simplified clear model was used: *I*) CRU; *II*) its conventional representation; *III*) IPN made up of two networks *II*].

Here it will be more convenient to invoke ordinal Latin prefixes or, even better, the nomenclature of complex compounds.[29]

In considering vitreous borates, one cannot bypass the question of the so called "borate anomaly" (BA)—the changes in the properties of borates which are non-additive in terms of composition.[35,197] The extrema and inflections in the "composition–property" relations are located predominantly in the regions corresponding to the compositions $2M_2O.5B_2O_3$ and $M_2O.5B_2O_3$ (28.6 and 16.7 mole % M_2O) and for certain properties also when the M_2O content is 4 to 5 mole.[197] Among the different models of the structural

Table 5. Comparative analysis of certain vitreous and crystalline anhydrous borates (see also Table 7).

M_xO_y in the M_xO_y–B_2O_3 system	Limits of glass formation region, mole % M_xO_y (Refs.177, 178)		Crystalline compounds (Ref.179) formed at atmospheric pressure[a] in different composition ranges (mole % M_xO_y)										
	lower	upper	50	46.2	40	37.5	33.3	28.6	25	20.8	20	16.7	10
Li_2O^b	0	50	α-(XXXIV)	—	—	—	(XLVIII)	?	(XLIII)	—	?	—	?
Na_2O	0 $(67)^c$	30 $(72)^c$	α-Trimer (Ref.26) β-?	—	?	—	α-(LXXXI) β, γ-?	?	α-(LXXXIV) β-(LXXXIII) γ-?	—	α-(LXXVIII) β-?	α, β, γ-?	α, β, γ-?
K_2O	0	37	Trimer (Ref.26)	—	—	—	(LXXV)	—	?	(LXXXV)	?	α-(LIV) β-(LV)	?[d]
MgO	43.0	44.2	?	α-(XXXVIII) β-(XCI)[e]	?	—	(XLIX)	—	—	—	—	—	—
CaO	27.1	41.1	Phase I (XXXV)	—	(LXXVII)	—	Phase I-? II-(LXXVI)	—	?	—	—	—	—
SrO	24.2	43.0	Phase I-?[f]	—	—	—	(XCVII)	—	?	—	—	—	—
BaO	17.0	39.8	α-? β-Trimer (Ref.26)	—	—	—	(LXXXII)	?	—	—	(LXXX)	—	—
Tl_2O	0	44.5	?	—	—	—	α, β, γ-?	—	?	—	?	?	—
La_2O_3	10.0	28.2	(XXXVII)[g] (XXXVIII)	—	—	—	—	—	(LXIV)	—	—	—	—
ZnO^h	44.0	63.6 (79.6)	α, β-?	?	—	—	(LI)	—	?	—	—	—	—
CdO	18.9	55.0 (85.4)	—	(XCV)[i]	?	—	(LII)	—	—	—	—	—	—
PbO^k	20.0	76.5	?	—	—	—	(XCVIII)	—	—	—	—	—	—
Bi_2O_3	22.0	65.3 (85.0)	—	—	—	Pentomer (Ref.112)	—	—	(LXVIII)	—	?	—	—

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[a] The macroanions listed in Tables 3 and 4; the literature references are given to the monoanions and oligoanions; ?—the compound is known but its structure has not been elucidated; dash—there is no information about the formation of compounds; α-, β-, and γ- as well as phase I, II—the compound exists in different polymorphic modifications.

[b] Compounds belonging to the Li_2O–LiCl–B_2O_3 system are also present in the glass formation region; see compounds (LXXXVI) and (LXXXVII) in Table 4.

[c] The Na_2O–B_2O_3–CO_2 system (effect involving the retention of CO_2 in the structure of borate glasses containing more than 67 mole % Na_2O [180]).

[d] It is appropriate to make a comparison with the structure of caesium borate of the same composition—see compound (LXXIV) in Table 4.

[e] The MgO–$MgCl_2$–B_2O_3 system.

[f] Isostructural with $CaO.B_2O_3$-I according to some data.[26]

[g] The La_2O_3–B_2O_3–MoO_3 and La_2O_3–B_2O_3–WO_3 systems.

[h] For the last four systems, there is a possibility of the incorporation of Zn, Cd, Pb, and Bi into the structure of macroanions in the vitreous state, i.e. the formation of the corresponding copolymers.[7]

[i] The CdO–CdS–B_2O_3 system.

[j] The compound $6PbO.5B_2O_3$, consisting of oligoanions with $n = 10$, is also present in the glass formation region[113] (see Fig.8, E).

changes occurring under these conditions, Tarasov's model[184,199] with certain modifications, illustrated in Fig.14 (here N_4 is the fraction of BO_4 according to NMR data), is thought to be outstanding.[198]

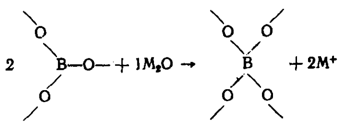
Table 6. The system of notation adopted in the chemistry of vitreous borates.[35]

Borate groups			Names of groups	Symbolic representation[a]
Fig.8	Fig.9	Fig.10		
A, a	—	—	Orthoborate	b'''
B, a	—	—	Pyroborate	b''_2
C	—	—	Cyclic metaborate	b_3
—	(XXXIV)—(XXXVIII)	—	Chain metaborate	b_∞
—	—	Subunit (LXXIV)	Boroxole ring[b]	a_3
—	(XLII) и (XLIII)	—	Triborate	a_2c
—	—	Subunit (LXXXI)	Triborate with one cyclic (non-bridging) oxygen ion	abc
—	—	Subunit (LXXV)	Di-triborate	ac_2
—	(XLVIII)—(LIII)	—	Diborate	a_2c_2
—	(LIV) и (LV)		Pentaborate	a_4c
—	—	Subunit (LXXXI)	Di-pentaborate	a_3c_2
—	—	(LXXVIII)	Tetraborate	a_6c_2

[a] Here a represents the BO_3 triangle with all the bridging (connecting) oxygen atoms, b, b'', and b''' represent similar triangles with one, two, and three terminal (non-bridging) oxygen ions, and c is the BO_4 tetrahedron with all the bridging (connecting) oxygen atoms [as in the CRU (XL) and (XLI) in Fig.9]. For example, the CRU (XLII) and (XLIII) in Fig.9 can be represented by the abbreviated formula a_2C.

[b] This is also the CRU in the layer network of vitreous B_2O_3 [1,35] (although it has been suggested[204] that the model in Fig.15c agrees best with experimental data in this case).

According to this model, as the M_2O/B_2O_3 ratio increases, the (B_2O_3) macromolecules, which are initially of the parquet type (Fig.14a), are cross-linked to form a three-dimensional network (Fig.14b) via the reaction[35]



$$2\ \geq B{-}O{-} + 1M_2O \rightarrow\ >B< \ + 2M^+$$

Next follows the accumulation in the network of non-connecting BO'_4 groups, i.e. the terminal $\geq B{-}O^-M^+$ groups (Fig.14c) with retention of the maximum density of cross-links attained in the region of x = 25 mole % M_2O. After this, the completion of the "accumulation" of BO'_4 is accompanied simultaneously by the degradation of the cross-links between the layers (Fig.14d). The latter then involves bonds between cyclochains in the layer, including the termination of the cyclochains themselves (Fig.14e). Finally, in the composition $M_2O.B_2O_3$, the small Li^+ ions are distributed freely at the terminal O atoms after the degradation of the polyboroxane layers into strips and chains and the capacity for their formation is retained (Fig.14f'). Under these conditions, as in the case of B_2O_3,[1] the CRU in the $Li_2O.B_2O_3$ chains in the vitreous and crystalline states are not identical, since in the former state N_4 = 33.3% while in the latter N_4 = 0. The larger Na^+ and K^+ ions break up the chain into segments as far as the formation of the corresponding cyclic trimers. The capacity for glass formation is then lost (Fig.14f''). Tarasov's model agrees with NMR data and explains satisfactorily a number of the changes in the properties of the vitreous borates.[7,184,200–202] At the same time it can be supplemented by taking into account the idea that some of the boroxole rings in the $B_2O_3)_C$ structure are opened,[1,203] particularly on passing to melts (Fig.15).[204] This is the reason for the larger set of CRU in the network and in the fractions of low-molecular-weight anionic groups in borate glasses.[35,200,205]

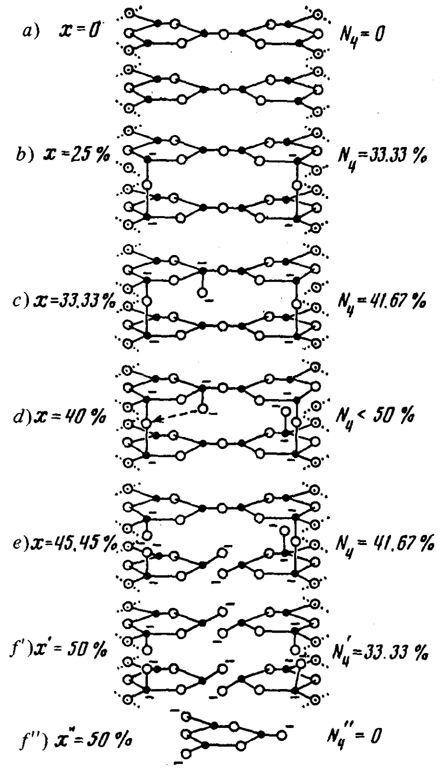


Figure 14. Tarasov's model for the cross-linking-degradation reactions of a network of borate glasses with M_2O contents in the range x = 0–50 mole % (according to Tarasov[184,199]).

This type of model does not exhaust the entire wide variety of mechanisms of the change in the long-range polymeric order in borate glasses (and the BA effect associated with it). For example, the interconversions of the one-, two-, and three-dimensional macroanions and their CRU can change as a result of hydrolysis (the properties of the glasses synthesised *in vacuo* and in air differ[197]). The fraction of the $\geq B{-}OH$ end groups (the changes in N_4 are not recorded by NMR) corresponding to 20% mole % M_2O can amount to only 0.002–0.004,[206] but this is not small, because even 0.01–0.1% of cross-linking (destructuring) agents are capable of influencing the course of macromolecular reactions.[189] Since vitreous borates are polyelectrolytes,[207] certain extrema (for example the solubility minimum) can be induced by passage through the isoelectric point (p*I*).[208] Since acid–base interactions are a fundamental concept in the chemistry of glass,[209] it is to be expected that additional structure-forming oxygen can be introduced into the glass network not only with M_2O (see Fig.14) but also directly from the atmosphere as N_4 is varied.[210,211] From the standpoint of the chemistry of macromolecular compounds, it is also not immaterial in what way the glass network has been formed: (a) by the fusion (congruent or incongruent) of the polymeric single crystal; (b) by the introduction of M_2O into the polymer $(B_2O_3)_c$ (Fig.14); (c) by synthesis from a charge containing monomeric $B(OH)_3$. In the latter case a series of macroanionic reactions, including polycondensation, BR effects (Section II), etc. take place. For example, a mixture of $Li_2O.B_2O_3$, $Li_2O.2B_2O_3$, and $Li_2O.4B_2O_3$ is formed at 873–1173 K from a mixture of H_3BO_3 and Li_2CO_3.[212] Although the exchange interaction[15] can lead to the formation of an equilibrium melt, it remains probable that different conformations of the macroanions, a distribution of their molecular weights, etc. will be observed under different cooling conditions in glasses with identical overall compositions.† Finally, changes in the structural organisation already at the polymeric-colloidal level can exert an appreciable influence on the properties of glasses,[181–183] as will be shown in the next Section.

Table 7. The phase separation regions and parameters in certain borate glass forming systems.[181]

M_xO_y in the M_xO_y–B_2O_3 system	Critical temperature, K	Critical composition (c_c), mole % M_xO_y	Liquidus temperature at c_c, K	Minimum temperature[a] T_{min}, K	Concentration range[b] for liquation at T_{min}, mole % M_xO_y
Li_2O[c]	726	4.5	1003	293	2—6 [224]
MgO	—	—	1415	1415	1.0—49.3
CaO	—	—	1248	1248	0.9—27.0
SrO	—	—	1213	1213	0—21.0
BaO	1423	6.9	1151	1151	0.7—16.3
Tl_2O_3	933 and 778[d]	48.2 and 4.1	809	873[e]	37.0—52.0
La_2O_3	—	—	1409	1409	1.5—21.5
ZnO	—	—	1235	1235	2.6—50.0
CdO	—	—	1253	1253	0.5—37.0
PbO	1060	9.4	1015	853	0.5—18.7
Bi_2O_3	—	—	982	982	2.0—19.0

[a] In the range investigated.

[b] Like the boundaries of the glass formation regions (Table 5), these boundaries depend on the method of observation and can differ from the data quoted here.[213] In particular, the electron paramagnetic probe method,[214] for example, EPR for Cu^{2+} and other ions,[215] reveals the presence in the optically transparent borate glasses of the region of the so called "EPR immiscibility".[216] In order to eliminate the latter, for example, in the K_2O–BaO–B_2O_3 system, the K_2O content should be ten times greater than that required for the elimination of opalescence.[216]

[c] A "pseudophase" structure,[224,225] resembling structures of the phason type, known in the colloid chemistry of polymers[183] and intermediate between the classical one- and two-phase structures, has been discovered in alkali metal borate systems with Na_2O and K_2O.

[d] The system has two critical points—the upper point in the region of stable liquation and lower point in the region of metastable liquation.

[e] The temperature at which the region of liquating compositions is widest.

3. Oxoborate Melts

Melts of low-molecular-weight anionic borates are typical ionic liquids: they expand with increase of temperature and their viscosity falls, while on cooling they readily crystallise without passing to a vitreous state. On the other hand, monophase and multiphase glasses, polycrystalline sitalls, and polymeric single crystals can be obtained from melts of macroanionic borates (i.e. glass-forming melts) when the composition and conditions are varied.

Table 7 indicates the regions and parameters of phase separation in certain borate glass forming systems.[181] The table shows that phase separation is manifested for low contents of M_xO_y in B_2O_3. The latter does not exhibit microheterogeneities other than thermal density fluctuations.[217]# The characteristic LAX [220] and light scattering[221] "flash" on passing to a melt is gradually abolished and the state usual for thermal density fluctuations obtains. The content of M_xO_y less than 25 mole % in the melt is apparently insufficient for the formation of the structure, illustrated in Fig.14b, throughout the bulk of the melt. New CRU, stabilised by the metal cations, arise in the B_2O_3 matrix (Fig.15). These CRU form individual blocks in the B_2O_3 matrix (this is indicated by the low-frequency branch of the Raman spectra[200,222]) connected to the CRU of the matrix via B–O–B linkages. Ultimately the "network" is found to be made up of CRU blocks of different chemical nature. In the colloid chemistry of polymers[183] such systems (of the type of network polyblock polymers or IPN)§ are treated as multicomponent polymer mixtures as regards phase separation. Phase separation in such mixtures proceeds via binodal (nucleation and growth) and spinodal mechanisms. The phase decomposition mechanism is known[183] to influence the morphology of the polymeric-colloidal structures formed.

The nucleation and growth mechanism	Spinodal mechanism
1. The composition of the second phase remains constant and invariant in time (equilibrium phase).	1. Before the attainment of equilibrium, there is a continuous change in composition.
2. The interface between the growing phase and the matrix is sharp.	2. The interface is diffuse and only gradually becomes sharp.
3. There is a distinct tendency towards a statistical distribution of the sizes and positions of the particles of the equilibrium phases.	3. A definite regularity arises in the sizes and distribution of the segregated phases.
4. The particles of the segregated phases tend to become spherical and only weakly interconnected.	4. The separated phases are usually non-spherical and are highly interconnected.

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† Effects similar to BA (as well as BR) are not a unique feature of borates and are manifested also in phosphate, inverted silicate, and other oxide glasses.[197]

We have in mind a preparation obtained from an evacuated melt. The presence of H_2O entails, according to low-angle X-ray diffraction (LAX) data,[217] the appearance of 25–30 nm heterogeneities, which is correlated with electron-microscope observations[218] and is reflected in a change of the rheological properties[219] (the appearance of a yield point and a decrease of viscosity). A decrease of viscosity is characteristic of only low (<0.3 mole %) H_2O contents, while an increase of the water content to >0.5 mole % inhibits such decrease.

§ A characteristic feature of macromolecular networks is the presence of rings in the latter and also a globular supermolecular organisation.[223] This is probably valid also for macroanionic networks.

The rheological, electrical, optical, diffusion, and chemical properties of borate melts and glasses, their glass points, densities, thermal expansion coefficients, capacity for crystallisation, etc. depend in their turn on the character of the phase distribution.[181,182] Hence the importance of taking into account the polymeric-colloidal aspect in synthesising vitreous materials with specified properties becomes clear.

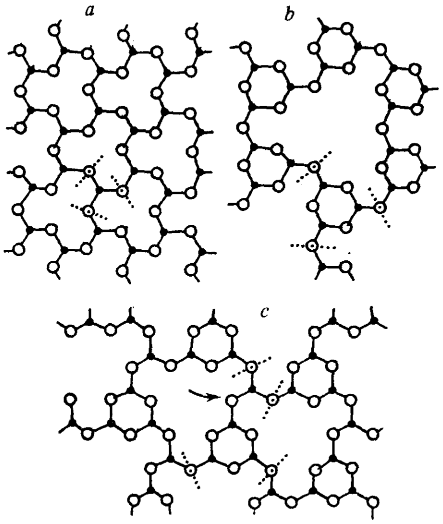

Figure 15. Quasi-crystalline models for the B_2O_3 melt:[204] a) $[BO_{1.5}]_{nn}$; b) $[B_3O_{4.5}]_{nn}$; c) $[B_3O_{4.5}\cdot BO_{1.5}]_{nn} = [B_4O_6]_{nn}$; the last model agrees best with the experimental data.

Together with features which they have in common with polymer mixtures, systems of the type of network polyblock polymers and IPN are also characterised by features such as the presence of chemical and real spinodal curves. For systems with an upper consolute point (UCP), the latter passes below the chemical spinodal curve, so that the region of unstable states under the real spinodal curve can be altogether inaccessible.[183] In the region between the chemical and real spinodal curves lie dissipative systems of the phason type, which are intermediate between the classical one- and two-phase systems. These apparently include also the so called "pseudophases" [224] and "modulated structures" [225] observed in borate melts and glasses. On ultracentrifugation of the melts,[182,226] the compositions of the separated phases correspond to those expected on the basis of the phase diagrams. Numerous examples of the practical applications of phase separation in glasses, including the so called precondition for the formation of sitalls,[228] are known.[227] The heat treatment of borate glasses designed to convert them into sitalls is carried out at 1023–1173 K (Ref.228, p.410). If polycrystalline sitalls are obtained in the presence of not less than 10^{12} prenuclear centres in 1 cm^3 of the volume, then the synthesis of polymeric single crystals requires the directional growth of one or several nuclei (see the original communications quoted in Tables 3 and 4). In general, the rate of growth changes from 2 [$PbO.2B_2O_3$—(XCVIII) in Table 4] to approximately 3000 μm s^{-1} [$Li_2O.2B_2O_3$—(XLVIII) in Table 3 [229]].

4. Oxoborates in the Gas Phase

Above the UCP, the glass-forming melts are homogenised evidently as a consequence of the decrease of the molecular weight and of the degree of polymerisation with increase of temperature. The presence of M_xO_y [230,231] as well as H_2O [1,232] in the B_2O_3 melt promotes its thermal degradation with transfer to the gas phase of low-molecular-weight anionic metal oxoborates[233–239] or of the low-molecular-weight fraction of hydrogen oxoborates.[1] Graft copolymerisation of the latter with various oxide substrates[11–13] makes it possible to achieve the chemical moulding of joints and coatings,[240–243] which has an advantage over the traditional technology in that it is possible to avoid laborious operations involving the processing of a macroanionic substance, since the synthesis of the polymer is combined with its moulding. As a consequence of the heterodiffusional character of the polymer formation reaction,[244] reactions of this type made it possible to achieve a gradient anisotropy of properties (refractive index, coefficient of thermal expansion, etc.) with respect to thickness. Special procedures for the formation of boron–oxygen monomers in the gas phase are also used in establishing a refractive index gradient in the manufacture of articles for fibre and integrated optics.[245,246]

IV. CONCLUSION

The question arises how one can account for the wide variety of borate macroanions which can be different for borates having identical chemical compositions. It is known that the unique nature of the macroanions and macromolecules is determined by the following criteria: (1) chains (layers, networks) of atoms or groups of atoms (CRU) linked by directional, predominantly covalent,¶ bonds can be discovered in their structure by one method or another;[1,185] the capacity for the formation of such chains (layers, networks) is determined by the structure of the electron shells of the corresponding atoms, i.e. by their position in the Periodic System of the Elements;[6,184] (2) the set of their properties does not change appreciably with decrease (increase) in the size of the chain (layer, network) by one or several CRU.[1,27] Such chains (layers, networks) are to some extent flexible due to the retention of the rotational degrees of freedom of the constituent units,[248] which is achieved in polyelementoxane macroanions as a result of a

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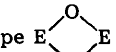
¶It has been suggested[247] that a given chain (layer, network) is polymeric provided that the degree of covalence of the bonds between the atoms in it is not less than 50% (52, 65, 68, 71% respectively for Al–O, Si–O, B–O, and P–O) or in the case of magnesium–oxygen polymers it can even be as low as 43%. Apart from electronegativity, the decrease of the entropy of a particular element with increase of the degree of polymerisation, i.e. of the number of covalently bound atoms, can serve as a measure of the degree of covalence of bonds.[247]

change in the bond length and valence angles in the E–O–E p-bridges (E = Si, B, P, Al, etc.).[184,191] This ensures a fairly large set of conformations in the given macroanions (a physical change in the steric form) and configurations (a change in form accompanied by a chemical reaction, i.e. by at least one transposition of bonds or valence angles). Hence one can understand not only the ability of the macroanions to pass to the vitreous (and for linear and layer macroanions also the highly elastic) state[184,191] but also their ability, familiar in crystal chemistry,[249] to "become adjusted" to the cationic component of the structure, i.e. their ability to alter, as the nature of the cations is altered [or, for the same cation, when the conditions of synthesis are changed—see, for example, (LXXXIII) and (LXXXIV) in Table 4], their configuration at all levels of the structural hierarchy—from CRU (including the formation of the "bow-shaped" configurations  and bridges of the type  [249]) to a superanionic organisation (the formation of IPN). In anhydrous compounds the requirements for the flexibility of the macroanion are enhanced, as increase in degree of hydration entails the appearance of the possible coordination of the cations not only to the $>\!E{-}O^-$ end groups or the connecting $-\overset{|}{\underset{|}{E}}{}^{-}-$ groups but also to the oxygen of water with subsequent damping [?bonding (Ed.of Translation)] via hydrogen bonds to the anion.[36,250]

As a result of the non-directional nature of the ionic bond, the cations always tend to become surrounded by the maximum number of counter-ions. For this reason, in the structural† sense, cationic constructions constitute a conservative, rigid base of substances with element–oxygen macroanions.[249] On the other hand, the macroanions are a component of the structure of such substances, which is variable and responds to a change in the nature of the cation and external conditions. Their configurational and conformation statistics are determined by O atoms in a state intermediate between the sp^2- and sp-hybridisations with atoms of other elements[251] and ultimately determines both the wide variety of borates, silicates, phosphates, and similar compounds and many of their properties.

This justifies the assumption that the development of the chemistry of these substances, which are widely distributed in nature and are used in technology, will be determined by the advances in their polymer chemistry. The *chemistry of macroanions*, which, in contrast to the macromolecular chemistry of carboatomic compounds, is still an inadequately developed albeit a promising field of polymer chemistry, comes to the fore for such substances. For the development of this field, it appears useful to employ a combined approach the necessity for which has been noted at the XXIInd Conference on the Chemistry and Macromolecular Compounds.[252] Its essential feature is as follows: since the unity of the material world is manifested in inorganic polymers, in order to reflect it adequately it is essential to achieve the symbiosis of various chemical disciplines, in the first place the macromolecular and colloid chemistry of polymers with inorganic chemistry. In this sense the present review (as well as the previous review[1]) should be regarded as an attempt at a practical realisation of this type of approach to borates and an attempt to present on this basis a sufficiently logical and well-founded picture of their structure, to demonstrate new ways of study, and to facilitate the prediction of the properties of technical materials and the improvement of the technology of their manufacture.

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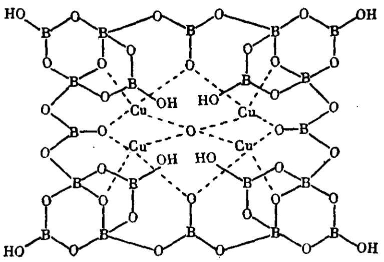
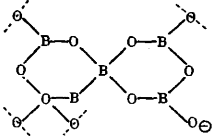
During the preparation of the manuscript for the press, a new monograph, devoted to inorganic polymers, was published.[253] Other publications[254,255] and the Russian translation of the IUPAC recommendations concerning the nomenclature of single-stranded and quasi-single-stranded inorganic polymers[256] attract attention in this connection. The choice of oxygen as a basis for the chemistry of non-carbon polymers has been justified[254] and a classification of the elements of the Periodic Systems in terms of their contributions to the structures of heteroatomic polymers has been developed.

During the same period, the family of oligoborates has been supplemented by a new representative $K_5H\{Cu_4O[B_{20}O_{32}.(OH)_8]\}.33H_2O$,[257] where n = 20. Ghose[258] examined the stereoisomers of the hilgardite network [(XVIII) in Table 1] with stereorepeating units made up of 1-, 3-, and 4-CRU.

Fig.9 may be supplemented by an example of a new pentaborate CRU ($3BO_3$ + $2BO_4$) with a single terminal (non-bridging) O atom:





while Table 3 may be supplemented by the corresponding example of a layer macroanion $[B_3^{III}B_2^{IV}O_8(O^-)]_{nn}^{3nn-}$, whose presence in the $CaNa[B_5O_9]_{nn}$ has been established,[259] and by yet another representative of phylloborates belonging to the $LnCo[B_5O_{10}]_{nn}$ group, where Ln = Yb.[260] Table 4 should be supplemented by new examples of boracites: $Fe_3Cl[B_7O_{13}]_{nnn}$ [261] and $Cu_3I[B_7O_{13}]_{nnn}$.[262]

Thermodynamic calculations have been carried out on the regions corresponding to the existence of various boron–oxygen monomers in the B_2O_3–H_2O vapour–gas phase at T = 300–1500 K at atmospheric pressure.[263]

The section on vitreous borates can be supplemented by data from a new review.[264] Detailed data on alkaline earth metal borates are described in a new monograph.[265]

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† But not in the chemical sense (for example, exchangeable cations).

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The Isomorphism and Catalytic Properties of Silicates with the Zeolite Structure

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The properties of a new group of catalysts based on crystalline silicates with the zeolite structure[†], containing the multicharged Be^{2+}, B^{3+}, Cr^{3+}, Fe^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Mo^{6+}, Se^{6+}, etc. cations occluded in the hydrothermal crystallisation process, are described. The state of the multicharged cations in the silicates has been characterised by physical methods (NMR, EPR, and X-ray diffraction). The selectivity and catalytic activity of such silicates in the formation and other reactions of hydrocarbons and hydrocarbon mixtures are examined.

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I. INTRODUCTION

According to Pauling's theory[1] and Tanabe's later revised versions,[2] the acid–base properties of binary oxides are determined by the incomplete compensation of the charges of the corresponding ions by the oxygen atoms in the environment. Any isomorphous heterocharge substitution of Si^{4+} cations in the silicon–oxygen skeleton of silicates by other cations of the type $Si^{4+} \rightleftharpoons M^{n+}$, where $n \neq 4$, should then impart to silicates a capacity for acid–base catalytic activity. Crystalline silicon oxides, including silicalite,[3] with an extensive system of pores are indeed adsorbents, but they do not possess catalytic properties. The catalytic properties of aluminosilicates, including zeolites, are determined by the fixation of aluminium cations in isomorphous positions in the silicon–oxygen skeleton as a result of the exchange $SiO_4^{4-} \rightleftharpoons AlO_4^{5-}$.

The idea that the above isomorphous heterocharge substitution takes place in zeolites, constituting a precondition for the formation of catalytically active centres, has been confirmed by a large number of data. For example, a dependence of the unit cell constant on the aluminium content in the zeolite crystals has been established.[4,5] It has been shown by ^{27}Al NMR that the vast majority of aluminium atoms in zeolites are in a tetrahedral oxygen environment.[6,7] It has been observed by ^{29}Si NMR [8-10] that the second coordination sphere of the Si^{4+} ion in the silicon–oxygen skeleton may contain between 1 and 4 aluminium atoms in groups of the type $[Si(OAl)_n]^{n-}$. A statistical model has been developed for the distribution of such groups with respect to the quantity n as a function of the overall aluminium content in the zeolite.[11] It was later suggested[7,12-15] that the change in the conditions of hydrothermal synthesis and in the subsequent treatment of zeolites can induce a deviation of this distribution from the statistical average in one direction or another.

It has been established that, as cations are eliminated[15,16] and also as a result of treatment of the specimens with acids,[17,18] $SiCl_4$,[19,20] and water vapour,[21,22] a signal with $\delta = -3-0$ p.p.m., assigned to Al atoms in an octahedral oxygen environment, i.e. outside the skeleton, appears in the ^{27}Al NMR spectra of zeolites together with a signal having the chemical shift $\delta = 55-61$ p.p.m. (which corresponds to Al^{3+} in a tetrahedral coordination with oxygen ions, i.e. in the silicon–oxygen skeleton. The solid-phase reactions

$$\underset{(I)}{[Si(OAl)_n]^{n-}} \rightarrow \underset{(II)}{Si[(OAl)_{n-1}]^{(n-1)-}} \frac{(n-1)}{3} Al^{3+},$$

leading to the appearance of the centres (II), probably occur during the cation elimination process ["decationation"] and in the course of thermochemical treatment. A group of type (II) can be regarded as a conjugate acid and base, capable of two-centre interaction with the reactant molecule. According to the literature,[12,15] the selectivity and stability of the catalytic action of zeolites depend both on the distribution of the groups $[Si(OAl)_n]$ with respect to n and on the concentration of groups of type (II).

Zeolites have found applications as catalysts in petroleum processing and in petrochemical processes. Different questions concerning their synthesis, investigation, and application have been considered in many reviews and monographs.[23-25] A series of studies devoted to new generation zeolites, of the ZSM type or pentasils, have been published during the last decade.[26,27] However, any zeolites constitute merely a special case of the manifestation of isomorphism, because they are all silicates with the same type of isomorphous substitution: $SiO_4^{4-} \rightleftharpoons AlO_4^{5-}$ or $Si^{4+} \rightleftharpoons Al^{3+}Na^+$.

A series of studies have been made in which silicates with the zeolite structure have been synthesised without adding sources of aluminium but in the presence of multicharged cations or Group I–VIII elements (M^{n+}), which created preconditions for the isomorphous substitutions $Si^{4+} \rightleftharpoons M^{n+}$ in the silicate skeleton formed.[23,28-30] This method of synthesis of silicates differs significantly from the methods of preparation of zeolites, in which multicharged cations are introduced by ion exchange. A zeolite behaves in ion exchange as a polyacid salt in which the chemical composition of the macroanion does not change and only the chemical nature of the cation, compensating for the negative charge

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[†] We shall henceforth refer to crystalline silicates with the zeolite structure, obtained under hydrothermal conditions from mixtures to which aluminium compounds had not been added before hydrothermal synthesis, as elementosilicates or ez-silicates.

of the skeleton, is altered:

$$[\mathrm{Si(OAl)}_n]^{n-}M_1^{n+} \xrightarrow[-M_1A^-]{+M_2A^-} [\mathrm{Si(OAl)}_n]^{n-}M_2^{n+}.$$

The state of the cations fixed in zeolites in this way has been characterised in a large number of studies[31-33] (see also the relevant reviews[25,34]).

The introduction of multicharged cations M^{n+} into the initial silica gel before its hydrothermal crystallisation leads to the possibility of altering the chemical composition of the anionic part of the silicon–oxygen skeleton:

$$[\mathrm{Si(OM)}_n]^{n-} \text{ and } [\mathrm{Si(OM)}_{n-1}]^{(n-1)-}\ \frac{n-1}{n}M^{n+}.$$

The uncompensated charge of the anionic component of the silicate and hence also the strength of the centres with acid–base properties should depend on the nature of the cation M^{n+}.

II. GENERAL RULES GOVERNING THE LIMITATION OF THE DEGREE OF ISOMORPHOUS SUBSTITUTION

The ideas about isomorphism are widely used in geochemistry and crystal chemistry. According to definitions,[35,36] isomorphism is a result of the capture of impurities in the course of the crystallisation of the system with substitution of some of the atoms by the impurity atom without change in the type of crystal structure of the original state. Approximate relations between the thermodynamic parameters of the system and the degree of isomorphous substitution have been examined in a review.[37] The principal postulates which must be taken into account in estimating the probability of isomorphous substitution reduce to the following:

1. By virtue of the existence of a definite relation between the enthalpy of formation of the system with isomorphous substitution and the ratio of the radii (R) of the interacting ions A and B, the limits of the mutual substitution are smaller the greater the difference between the values of R. It has been suggested[38] that the isomorphous exchange A $\rightleftharpoons$ B is possible provided that $\Delta R/R \leq 0.15$.
2. The ions A with larger R substitute the ions B with smaller R more readily than in the case where substitution is accompanied by a decrease in the coordination number of the ion A and, conversely, the substitution is more difficult if it is accompanied by an increase in the coordination number of the ion A.[38]
3. The limits of isomorphous substitution depend on the ratio of the electronegativities χ and ionisation potentials of the interacting ions.
4. In the isomorphous substitution A $\rightleftharpoons$ B there is a possibility of a shift of the central atoms with retention of the symmetry of the environment in the main system. The minimum in the free energy of the system is attained when the atoms A and B shift by $(0.025-0.03)R$.
5. Since the exchange A $\rightleftharpoons$ B does not alter the long-range electrostatic interaction, a long-range order in the disposition of A and B may be absent, but a short-range order should exist as a condition for the attainment of the energy minimum.[39]
6. The substitution A $\rightleftharpoons$ B can occur when the charges differ by 1, 2, and 3 units. The compensation of the excess charges generated can be non-local (via the formation of electronic and hole centres) and local, when a species with a balancing charge is located in the immediate vicinity to the excess charge. Local defects can have uncompensated magnetic moments and can interact with an external magnetic field, which leads to the possibility of their investigation by EPR.
7. The distribution of ions in the crystal lattice can be statistically uniform or non-uniform.[40,41]
8. The mutually substituting cations should be chemically inert in relation to one another.

Examples of pairs of cations whose mutual substitution can take place with a high probability have been published:[35] the substitution of Si^{4+} by the Ge^{4+}, Al^{3+}, Be^{2+}, Fe^{3+}, Ga^{3+}, P^{3+}, and Ti^{4+} ions is most probable for the $Si^{4+} \rightleftharpoons M^{n+}$ system.

The parameter ρ, introduced by Pauling,[1] can also be used as a criterion for the selection of cations capable of mutual substitution. By definition,[1] ρ is a criterion of the stability of the state of the cation in the given coordination environment and is a function of the attractive and repulsive forces of the ions in the first coordination sphere. To a rough approximation, ρ can be set equal to the ratio of the radii of the cation and anion. The critical values of the parameter ρ for oxides (ρ_c) outside the limits of which the coordination environment of the cation should change, calculated in accordance with Pauling's approximations, are listed in Table 1. The table also includes the values of ρ for different cations. [The ionic radii R taken from Bokii [42] and $R_{O^{2-}} = 1.36$ Å [43] were used in the calculation of ρ.)

Table 1. The parameter ρ for the M^{n+} cations.[1]

Group 1 ($\rho_c = 0.732$; C.N. = 8)		Group 2 ($\rho_c = 0.414$; C.N. = 6)		Group 3 ($\rho_c = 0.225$; C.N. = 4)		Group 4 ($\rho_c = 0.147$; C.N. = 3)	
M^{n+}	ρ	M^{n+}	ρ	M^{n+}	ρ	M^{n+}	ρ
Pb^{2+}	0.926	In^{3+}	0.676	Al^{3+}	0.419	B^{3+}	0.147
Sn^{2+}	0.750	Mn^{2+}	0.669	Mn^{4+}	0.382		
Tl^{3+}	0.772	Zn^{2+}	0.610	Ge^{4+}	0.323		
Nd^{3+}	0.73	Hf^{4+}	0.603	V^{5+}	0.294		
Eu^{3+}	0.71	Cu^{2+}	0.589	Si^{4+}	0.287		
		Sn^{4+}	0.492	Cr^{6+}	0.257		
		Fe^{3+}	0.492	P^{5+}	0.257		
		Mo^{6+}	0.478	Se^{6+}	0.257		
		Ti^{4+}	0.470	Be^{2+}	0.250		
		Pt^{4+}	0.470				
		Cr^{3+}	0.470				
		Sb^{3+}	0.470				
		Ga^{3+}	0.456				
		Sb^{5+}	0.456				
		V^{4+}	0.449				

According to Pauling's criterion,[1] only cations comprising Group 3 in Table 1 should be fixed in a stable tetrahedral environment. Vernadskii's isomorphous series, within the limits of which cations in natural formations are believed to be capable of isomorphous mutual substitution, is widely known: Si^{4+}, Al^{3+}, Ga^{3+}, Fe^{3+}, Cr^{3+}, V^{4+}, Mn^{2+}, Mg^{2+}, Ti^{4+}.[35] It is assumed[35] that, within a narrow range of concentrations of the substituting ion (less than 1 at.%), isomorphism is possible in virtually all inorganic compounds.

III. HYDROTHERMAL SYNTHESIS

The principal procedures in the synthesis of zeolites and ez-silicates are the same. The initial mixtures contain in both cases a source of silicon, alkali, and salts of multicharged cations but in the synthesis of elementosilicates a source of aluminium is not added. There is a possibility of synthesising elementosilicates incorporating simultaneously several types of cations, with the substitution $Si^{4+} \rightleftharpoons M_1^{n+} + M_2^{n+}$.

In the preparation of elementosilicates with the structure of zeolites of the pentasil or ZSM type, organic surfactants, namely quaternary ammonium bases, polyamines, aminoalcohols, alcohol, etc., are also introduced into the initial mixture. An aqueous silica sol, water glass, and silica gel are used as sources of silicon. A mixture consisting of a source of silicon, a source of M^{n+}, organic additives, alkali, and, sometimes, a seed is homogenised and then placed in an autoclave, where it is kept under hydrothermal conditions for 1–30 days at 80–200 °C. After the completion of crystallisation, the deposit is filtered off, washed, and dried. Before catalytic tests, the solid product is annealed at 520–550 °C in order to eliminate organic inclusions and cations are removed by treatment with $NH_4OH + NH_4Cl$ solutions or solutions of inorganic acid.

We shall consider briefly the characteristics of the chemical behaviour of the SiO_2–H_2O and SiO_2–M_nO_m–H_2O systems in hydrothermal treatment. It is known[44] that $Si(OH)_4$ coagulates in the range $6 < pH < 8$, dissolution and depolymerisation begin at $pH \geq 9$, while at $pH > 10.5$ complete depolymerisation of $(SiO_2)_n$ is observed. In the pH range from 12 to 13.56, the system contains predominantly disilicate ions of the type $[Si_2(OH)_{10}]^{2-}$ whereas at $pH \geq 13.83$ the monosilicate ions $[Si(OH)_5 2H_2O]^-$ predominate.

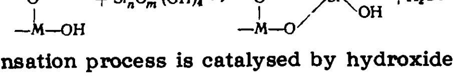
Thus polymerised silicon-containing ions of the type $[Si_nO_m(OH)_p]$, in which the coordination number of Si^{4+} is 4, predominate in aqueous media in the range $6 < pH < 10$. As a result of the surface reactions $[Si_nO_m(OH)_p] + 2OH^- \rightarrow [Si_nO_m(OH)_pO]^= + H_2O$, such species require a negative charge.

The polymerisation condensation of silicate ions includes reactions proceeding via an ionic mechanism with participation of OH^-. The condensation leads to the formation of siloxane linkages and the probability of the synthesis of cyclic structures is therefore high.

As a result of polymerisation condensation processes, silicate ions incorporating individual elements or individual structural blocks comprising crystalline varieties of silicates may be formed in an aqueous medium. Such structural blocks may be four- and six-membered rings of tetrahedra. The six-membered rings can be combined to form secondary structural blocks: an individual six-membered ring (beryl) and one-dimensional (amphiboles), two-dimensional (pyroxenes), and three-dimensional (elements of ultramarine, α-quartz, tridymite, and cristobalite) chains of rings.

The multicharged ions hydrolyse in aqueous solutions with formation of positively charged species and liberation of a proton to the outer sphere of the complex. The pK for the acid hydrolysis of multicharged cations have been published.[45,46] In alkaline media the hydroxides of Zn^{2+} and Si^{4+} are more basic than $Si(OH)_4$, while the hydroxides of the cations listed below are more acid, their acidity decreasing in the sequence $Ti^{4+} > Fe^{2+} \cong Fe^{3+} \cong Ga^{3+} > Th^{4+} > Al^{3+} > B^{3+} > In^{3+} > Si^{4+}$. The multicharged B, Ge, Tl, Cr, Mo, W, and V ions can hydrolyse with formation of negatively charged species. There is also a possibility of the polymerisation of hydroxides with formation of dinuclear and polynuclear complexes.[47]

The addition of metal salts facilitates the coagulation and polymerisation of silicate ions. In the presence of multicharged hydrolysed M^{n+} ions, the solubility of silicate ions falls in the first place owing to heteropolymerisation reactions:



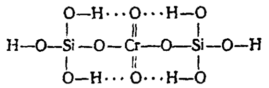
The condensation process is catalysed by hydroxide ions in this case also. The higher the charge of the ion, the greater its capacity for coagulation in relation to silica sol.

The Al^{3+} cation interacts most effectively with the monomeric silicate ion at pH 9. In the pH range 5–7, there is a possibility of the formation of the $[Al(OH)_2]^+$ and $[Al_2(OH)_5]^+$ ions. The complexes $NaAl_{13}(OH)_{32}(SO_4)_4(H_2O)_x$ are formed in the presence of SO_4^{2-}. The cation $[Al(OH)_4]^-$ is formed at pH 9–11.[47]

The interaction of Fe^{3+} with the surface Si–OH groups proceeds via heteropolymerisation processes, which has been demonstrated by the fact that at pH 6–8 the precipitation of $Fe(OH)_3$ on the macrosilicate ions is not observed in an SiO_2 containing system.[44]

As regards the character of its interaction with $(SiO_2)_n$, the cation Cr^{3+} differs greatly from Al^{3+}. The reason is that the chromite ion is not formed as readily as AlO_2^-; furthermore, Cr^{3+} is much larger than Al^{3+} and cannot be incorporated in the SiO_2 lattice with formation of stable anions.

The chromate ion, containing Cr^{6+}, retards the polymerisation of $Si(OH)_4$ at pH 0.5–3.0. It has been suggested[44] that the silicate ions dimerise in the presence of Cr^{6+} with formation of species of the type



The chemical properties of the Be^{2+} cation resemble those of Al^{3+}; solutions of beryllates, like those of aluminates, contain polymeric anions of the type $Be_2O_3^{2-}$ and oxo- and hydroxo-complexes. The hydrolysed Be^{2+} ion is capable of being strongly adsorbed on silica.[44]

The rate of interaction of silicic acid polymers with molybdic acid is higher the lower the molecular weight of the polymer. The interaction is preceded by the successive dissociation of the silicate ions to the monomer, which results in the formation of molybdosilicic acid.[44] The reaction of the silicate ion with H_3PO_4 represents condensation without the participation of water.[44] The Si–O–P and Si–O–B linkages hydrolyse in aqueous solutions. The precipitation of zinc salts by sodium silicate entails the mutual coagulation of zinc hydroxide and silica without the subsequent crystallisation of an amorphous deposit.[48,49]

Table 2. Conditions in the synthesis of beryllosilicates with the zeolite structure.

Type of structure	Source of Be^{2+}	Source of Si^{4+}	t, °C	τ, days	SiO_2/BeO*	Refs.
D, orthorhombic	$Be(NO_3)_2 + NaAlO_2$	32% SiO_2 sol	175	2	12—60	[50]
Faujasite	$Be(NO_3)_2$	Na silicate	100	2	14.3	[51]
Zeolite Y	$NaBeO_2$	Na silicate	70—130	1—2	10	[52]
Faujasite	$NaBeO_2$	SiO_2 sol	70—100	2	—	[53]
Zeolite A, X	—	—	100	2—5	2.5—6.0	[54, 55]
TRS-27, -41, -42	$Be(NO_3)_2$ in alcohol***	TEOS**, SiO_2 sol	155—200	0.5—1.0	12—100	[56]

*Molar ratio in solid product.

**TEOS = tetraethyl orthosilicate.

***Organic additives—tetrapropylammonium hydroxide and triethanolamine.

Thus, when the precipitation process is carried out in the range of mixture compositions and pH in which zeolites are formed, the sources of Si^{4+} and M^{n+} enter into the composition of polymeric blocks. The heteropolymerisation takes place via the interaction of polymers. The direction of this interaction depends on (a) the ratio of the basicities of the polymers containing Si^{4+} and M^{n+}, (b) the sign and charges on the species, and (c) the degree of polymerisation and dehydration of the monocationic polymers in the initial mixture for hydrothermal synthesis.

On the basis of general considerations, one can assume that the synthesis of the crystalline silicate should be preceded by the following stages: (1) the hydrolysis of the source of M^{n+} and the formation of monocationic polymers containing the Si^{4+} or M^{n+} ions; (2) the heteropolymerisation of the monocationic polymers; (3) their depolymerisation; (4) the oriented fixation of the polymeric blocks accompanied by the establishment of long-range order in the arrangement of ions in the skeleton.

The rate of crystallisation of the silicate system should depend on the ratios of the rates of processes involving the aggregation of the polymeric species, on the one hand, and their depolymerisation and orientation, on the other. The depolymerisation and reorientation stages require a definite activation energy and their rate should therefore increase with increase in the temperature of the hydrothermal treatment and should also depend on the presence of an initiator and, what is especially important, on the nature of the ion-transferring component. The rate of reorientation of the blocks is higher the larger the polar species of the deposit

Table 3. Conditions for the synthesis of borosilicates with the zeolite structures.

Type of structure	Source of B^{3+}	Source of Si^{4+}	Organic additive	t, °C	τ, days	SiO_2/B_2O_3	Remarks	Refs.
Zeolites A, X, and P, H-sodalite, analcime	borosilicate glass	Na silicate	—	80	7—9	—	—	[57]
Zeolite A	Na_3BO_3	Na silicate	—	45—170	—	1.78	—	[58]
Faujasite	B_2O_3	—	—	—	—	0.24—2.02	—	[59]
Faujasite	Borosilicate	kaolin, quartz	—	1100	0.02	—	—	[60—62]
Zeolite-like	$B^{3+}+Al(OH)_3$	aerosil	HMDA	100—200	5	145	conversion of methanol into unsaturated hydrocarbons	[63]
Pentasil	$H_3BO_3+Al(OH)_3$	aerosil	HMDA, DPDA, TEDA, PDA, DETA	150	5	33	synthesis of olefins from methanol and dimethyl ether	[64, 65]
—	B_2O_3	soluble glass	MEA	170	1	—	carrier, adsorbent	[66]
ZSM-5	—	—	—	—	—	31.7	conversion of methanol and ethylene into aromatic and aliphatic hydrocarbons	[67]
ZSM-5	borosilicate glass	—	HMDA	150	5	168	reforming, alkylation	[68]
Borolite: A, B, ..., I, AMS-1, -11, -12	H_3BO_3	TEOS	TPAOH, TEAOH, TBABr, EDA	150—170	6—17	4—13.9	cracking, hydrocracking, isomerisation of xylenes	[69, 70]
AMS	H_3BO_3	30% SiO_2 sol	TPABr	165	7	—	isomerisation and disproportionation of C_2 and higher hydrocarbons	[71]
Eu-1, Eu-2	—	solid SiO_2	HMDA derivative	85—250	1—30	—	separation of aromatic hydrocarbon	[72, 73]
Pentasil	H_3BO_3	silica sol	TPABr	165	7	44.4—104.5	isomerisation of xylenes	[74]
ZSM-5	H_3BO_3	40% SiO_2 sol	EDTA + TPA	168 166 185	7 10 3.5	—	conversion of methanol into dimethyl ether	[75]
ZBM-30	H_3BO_3	SiO_2 (pyrogenic)	DPDA, TEDA, PDA, DETA	170 200	5 0.5	80	synthesis of olefins from methanol and dimethyl ether	[76]
ZHB	H_3BO_3	aerosil	DEG, TEG, HMDA	80—200	0.5—5.0	10—50	conversion of hydrocarbons	[56, 77, 78]

Notation: TEOS = tetraethyl orthosilicate, HMDA = hexamethylenediamine, TPAOH = tetrapropylammonium hydroxide, TEAOH = tetraethylammonium hydroxide, TBABr = tetrabutylammonium bromide, EDA = ethylenediamine, TPABr = tetrapropylammonium bromide, DPDA = dipropylenediamine, TEDA = triethylenediamine, DEG = diethylene glycol, and TEG = triethylene glycol.

or the larger the charge of the elementary blocks.[48] The nature and concentration of the sources of the multicharged ions as well as the nature of the organic additives playing the role of ion-transferring agents therefore influences strongly the crystallisation of silicates with a particular structure.

The conditions for the synthesis of silicates described in the literature are described systematically in Tables 2–6. In the synthesis of beryllosilicates (Table 2), the source of beryllium employed is its nitrate or sodium beryllate, while the source of silicon is silica sol or sodium silicate. The reactant ratio and the crystallisation temperature influence the type of crystal structure of the final product. The crystalline zeolite-like orthorhombic silicate with a SiO_2/BeO ratio of 12–60 has been obtained by the hydrothermal treatment of a mixture consisting of sodium aluminate, beryllium nitrate, and an aqueous solution of silica sol for 24 h at 175 °C.[50] Silicates with structures of type A, X, and Y zeolites have been obtained by the crystallisation of mixtures of definite composition at 70–130 °C.[51–55] A zeolite, designated by TRS, with the ratio $SiO_2/BeO > 12$ in the solid product (of the ZSM type), has been obtained from a mixture of beryllium nitrate and tetraethyl orthosilicate in the presence of tetrapropylammonium hydroxide in an alcoholic medium over a period of 12–17 h at 155–200 °C.[56]

Table 3 presents the conditions for the synthesis of borosilicates, the composition of the solid phase synthesised, and also the reactions in which silicates have been investigated. A borosilicate of the type of a zeolite with the ratio $SiO_2/B_2O_3 = 1.78$ has been obtained from sodium silicate and borate at 45–170 °C.[57–59] A zeolite of the faujasite type has been synthesised from a mixture of borosilicate, boron oxide, kaolin, and quartz after it had been sintered at 1110 °C.[60–62] High-silica borosilicates with the structure of pentasils[63–78] have been obtained by the crystallisation at 150–170 °C of mixtures incorporating a source of boron (H_3BO_3), freshly prepared aluminium hydroxide, aerosil, and organic amines. The use of monoethanolamine[66] and hexamethylenediamine as the organic compound together with borosilicate[67,68] glass or soluble glass enabled the authors to obtain zeolites of the ZSM-5 type.

The main conditions for the synthesis of silicates with the zeolite structure, containing Group III, IV, V, and VI elements, are presented in Table 4. Numerous phosphorus-containing silicates with the analcime, chabazite, phillipsite, sodalite (HS) and type A, X, Y, P, and L zeolite structures have been synthesised.[79–81] The crystallisation was carried out from the gel at 80–200 °C using reactive phosphorus-containing compounds as the sources of phosphorus, usually orthophosphoric acid. The presence of an organic compound [tripropylamine (TPA)] in the crystallising system promoted the crystallisation of a silicate with the type ZSM zeolite structure.[82,83] A sulphur-containing zeolite has been obtained by introducing sulphuric acid into the crystallising mixture instead of phosphoric acid.[82] Silicates with the ZSM structure have also been obtained from systems incorporating silica sol, TPABr, hexamethylenediamine (HMDA), and also arsenic, tin, indium, or tellurium salts.[83,85–88] A zeolite-like silicate, whose composition incorporates iron and arsenic cations, is formed in an acid medium at 220 °C.[84]

Gallo- and germano-silicates (Table 5) were synthesised for the first time from aqueous solutions of sodium gallate and germanate and silica sol at 100 °C.[90] The silicates obtained proved to have the same structures as zeolites X, A, and P and thomsonite, which was demonstrated by X-ray diffraction. It was noted that zeolite A crystallises only from sodium aluminogermanate gels, while zeolite X crystallises from a mixture of sodium gallogermanate and sodium aluminogermanate. Zeolite P is formed on recrystallisation of zeolite A in an alkaline solution.[90] An analogue of zeolite X has been obtained from sodium metasilicate and $GaCl_3$ in an alkaline solution.[91,93–95] The zeolite chabazite has been synthesised from the potassium galloaluminosilicate system, while phillipsite has been obtained from the sodium gallosilicate system.[96,97]

The crystallisation of $HGaCl_4$ and sodium silicate for different periods at 200 °C is accompanied by the formation of several types of zeolites.[92] Analogues of faujasite having the aluminosilicate composition have been obtained in an alkaline medium from sodium and potassium germanates at temperatures not above 100 °C,[93–95,98–100] Zeolites of the

Table 4. The principal conditions for the synthesis of silicates with zeolite structures containing Group III, IV, V, and VI elements.

Element introduced	Type of structure	Source of M^{n+}	Source of Si^{4+}	Organic additive	t, °C	τ, days	SiO_2/M_nO_m	Refs.
P(Al*)	analcime	H_3PO_4 + Al, Na phosphates	SiO_2 (colloidal)	—	230—450	1—68	—	[79]
P	zeolites X, Y, A, L, P, S, and HS	K_3PO_4	clays, zeolite	—	230—530	4—5	—	[80]
P	analcime, chabazite, zeolite A, phillipsite	H_3PO_4	**	—	60—70	—	—	[81]
P	zeolite Y, ZSM-5	H_3PO_4	40% SiO_2 sol	TPABr	145	2	—	[82]
P	ZSM-5	PCl_3	zeolite	TPABr	150	0.05	12	[83]
S	ZSM-5	H_2SO_4	40% SiO_2 sol	TPABr	145	2	—	[82]
As	OTW	KH_2AsO_4, As ferrite	SiO_2	—	220	0.05	—	[84]
As	ZSM	As_2O_3	aerosil	HMDA	150	5	1380	[85]
Sn	ZSM	$SnCl_4 \cdot 5H_2O$	SiO_2 (colloidal)	TPABr	150	1	32	[86, 87]
Te	ZSM	H_6TeO_6	SiO_2 (colloidal)	TPABr	150	1	32	[88]
Pb	faujasite	$PbSiO_3$	Na silicate	—	100	4	—	[89]
In(Ce*)	ZSM	$In_2(SO_4)_3$	SiO_2 sol	TPABr	150	0.05	12	[83]

*Introduced together with the element.

**Synthesis carried out by the coprecipitation method.

type of pentasil and ZSM-11 crystallise at 150 °C in the presence of HMDA and tetrabutylphosphonium chloride respectively.[72,73,103]

Table 5. Conditions in the synthesis of silicates with the zeolite structure containing the Ga^{3+} and Ge^{4+} cations.

Type of structure	Source of M^{n+}	Source of Si^{4+}	Organic additive	t, °C	τ, days	SiO_2/M_nO_m	Refs
Thomsonite, zeolites A, X, and P	Ga_2O_3, GeO_2	—	—	100—200	3	—	[90]
Analcime, natrolite, nepheline, gismondine, H-sodalite	$HGaCl_4$	Na silicate	—	200	5—10	—	[92]
Zeolite 13X	$GaCl_3$	Na silicate	—	102	0.25	2,6	[91]
Zeolite A	Ga_2O_3 $Ga(OH)_3$	Na silicate SiO_2 sol	— —	150 93	7 12	5 4.5	[93]
Zeolite 13X	Na gallate	SiO_2 sol	—	170	3	5	[94, 95]
Chabazite	K gallate	K silicate	—	100	7	—	[96]
Phillipsite	Na gallate	Na silicate	—	100	7	—	[97]
Faujasite	GeO_2 in KOH	—	—	90	2.5	2.02	[98]
Faujasite	Ge^{4+}	—	—	—	—	—	[100, 101]
Zeolite	Ga^{3+} substitutes Al^{3+}	Ge^{4+} substitutes Si^{4+}	—	—	—	—	[102]
ZSM-11	Ga^{3+} substitutes Al^{3+}	Ge^{4+} substitutes Si^{4+}	TBP	150	4	—	[103]
Eu-1, Eu-2	Ga^{3+}, Ge^{4+}	solid SiO_2	HMDA	85—150	1—30	—	[72, 73]

Notation: TBP = tetrabutyl phosphate; HMDA—see reference to Table 3.

The data in Table 6, where the conditions in the synthesis of silicates crystallising in the presence of transition metal cations and platinum group elements are presented,[104–128] permit the following conclusions. The crystallisation of a silicate system, into the composition of which the above cations have been introduced together with quaternary ammonium compounds, leads to the formation of systems isostructural with type ZSM zeolites in alkaline media at 100 °C and above. The sources of cations are their salts and oxides and acids based on them. The sources of silicon and organic ions are the reagents indicated in Tables 2–5.

The characteristic features of the crystallisation of silicates in the presence of multicharged cations have been studied systematically as a function of the nature and content of the latter.[129–137] The influence of the temperature, crystallisation time, component ratio, and the nature of the modifying cation on the content of the zeolite-like silicate phase has been investigated. For the ratios $OH/SiO_2 = 0.1–0.2$, $TBABr/SiO_2 = 0.11–0.15$, and $H_2O/SiO_2 = 20–50$ and temperatures in the range 140–200 °C, the silica sol crystallises predominantly with formation of a product having the X-ray diffraction parameters of a type ZSM-11 zeolite regardless of the nature of the source of M^{n+}. In many cases the solid product may contain α-quartz or an amorphous phase depending on the temperature, crystallisation time, and the type of cation. With increase of crystallisation temperature from 140° to 200 °C for the same crystallisation time, the constant of the crystalline zeolite phase (CZP) passes through a maximum in the range 140–150 °C in many cases (Fig.1). As the CZP crystallisation temperature increases further, the content of α-quartz diminishes and increases. This result confirms the available data showing that the zeolite phase is formed as an intermediate in the hydrothermal treatment of the $SiO_2–H_2O–M(OH)_m$ system; after a time, it recrystallises and denser and thermodynamically more stable structures, including α-quartz, are formed.[23]

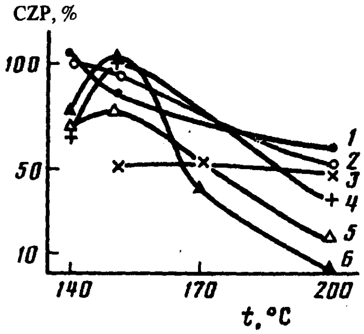


Figure 1. The influence of the temperature of the hydrothermal treatment (t, °C) of silica sol on the content of the ZSM-11 phase in the solid product obtained after the introduction of various cations M^{n+}: *1*) Mn; *2*) Cr; *3*) Eu; *4*) Fe; *5*) Cu; *6*) Zn.[133]

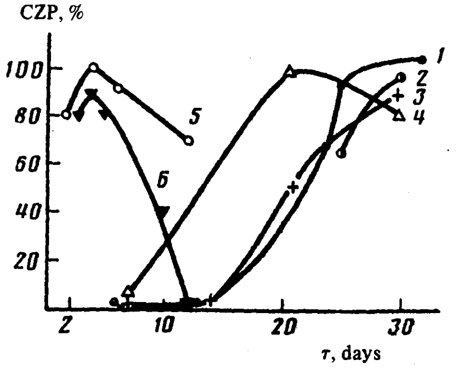


Figure 2. The influence of the duration of the hydrothermal treatment (τ, days) on the content of the ZSM-11 phase in the solid product obtained after the introduction of various cations M^{n+}: *1*) Ti; *2*) Cr; *3*) Cu; *4*) Zn; *5*) B; *6*) Eu.[137]

Changes in the CZP content of the same character are observed after an increase in the duration of the hydrothermal treatment of silica sol, keeping the temperature and the composition of the initial mixture unchanged (Fig.2): the content of the ZSM phase usually increases during the first 2–5 days and then gradually diminishes.[133]

A common feature is the decrease of the content of the ZSM phase with increase of the amount of M^{n+} in the initial mixture (Fig.3); this means that the crystallisation reactions of silicate ions are retarded in the presence of M^{n+}.[44] The cause of this phenomenon has not been investigated in detail. However, presumably in the presence of the M^{n+} hydrolysis product either the solubility of the silicate increases or the degree of coagulation diminishes and the stability of the silica sol increases as a result of the adsorption of the $[M_nO_m(OH)p]$ groups on the surface of the polymeric species of the silicate system. The adsorbed polymeric ions containing M^{n+} can prevent the establishment of long-range order in the silicate system.

According to Pauling's criterion, stabilisation in an eight-membered oxygen environment is most likely for the cations in groups 1 (Table 1). It has been shown[137] that most of

Table 6. Principal conditions for the synthesis of silicates with zeolite structures containing transition elements.

Element	Type of structure	Source of M^{n+}	Source of Si^{4+}	Organic additive	t, °C	τ, days	SiO_2/M_nO_m	Refs.
Ti	silicate	$TiOCl_2$	Na silicate	—	95	1,5	5—20	[104, 105]
	TRS-1 . . .TRS-64	$TiOCl_2$, TE-Ti, $TiCl_4$	TEOS	TPAOH	145—175	10	3	[106]
Ti	ZSM-5	$TiCl_4$	SiO_2 (pyrogenic)	HMDA	100—200	0,5—5	—	[76]
V(Al)	VK-2	V_2O_5	Na silicate	—	60	2,5	2—4	[107]
V	zeolite	VCl_3	soluble glass	HMDA	150	5	127	[108]
V	ZSM-5	V_2O_5	Na silicate	TPABr	96	5—6	—	[56]
V	TRS-48	H_4VO_3	TMOS	TPAOH	175	6	17	[106]
Cr	silicate	Cr_2O_3	chabazite	—	100	—	—	[109]
Cr	ZSM-5	$CrK(SO_4)_2$	Na silicate	TPABr	96	5—6	—	[110]
Cr	TRS-28	$Cr(NO_3)_3$	TEOS	TPAOH	155	13	38	[106]
Cr	zeolite-like	Cr sulphate, hydroxide, and oxide	soluble glass	HMDA	150	5	164—399	[111, 112]
Cr	AMS-1	$NaCrO_2$	30% SiO_2 sol	TPABr	150	2—20	16	[113]
Cr	CZS	Cr nitrate and sulphate	SiO_2 sol	TPAOH	165	15	—	[114, 115]
Fe	—	ferroalloy	SiO_2 (dust)	—	100	0,5	—	[116]
Fe	silicate	Fe_2O_3	chabazite	—	100	—	—	[109]
Fe	zeolite-like	Fe-phosphoric acid	—	—	350	1	1	[117]
Fe	zeolite	Fe nitrate	SiO_2 sol	TPAOH	148	2	32	[118—120]
Fe	zeolite	Fe sulphate, oxide, and hydroxide	soluble glass	—	150	5	81	[121—123]
Fe	ZBM-30	Fe sulphate and oxide	SiO_2 (pyrogenic)	HMDA	170	5	—	[124]
Ni	ZSM-5	Ni nitrate	SiO_2 (colloidal)	TPABr	100	19	160	[125]
Co	ZSM-39	$Co[Co(NH_3)_2]^+$	SiO_2 (colloidal)	C_4H_8NH	210	5	—	[126]
Zn	A	Na_2ZnO_2	Na metasilicate	—	95	—	1—1,5	—
Zn	ZSM-5	Zn nitrate	SiO_2 (colloidal)	TPABr	100	14	50	[84]
Zn	TRS-66	Zn nitrate	TEOS	TPAOH	197	6	15	[106]
Zn	ZSM	$Zn_2B_6O_{11}$	Na silicate	TPABr	96	5—6	—	[56]
Zr	silicate	$ZrOCl_2$ (KOH)	Na silicate, SiO_2 sol	—	200	1,5	—	[104, 105]
Zr	ZSM	ZrO_2	SiO_2 (colloidal)	TPABr	150	25	—	[121]
Zr(Al)	zeolite	$ZrOCl_2 \cdot 8H_2O$	Na silicate	TPAOH	160	5	—	[127]
Mo(Al)	silicate	MoO_3	Na silicate	—	100—160	2	150	[128]
Mo	ZSM	H_2MoO_4	SiO_2 sol	TPABr	96	5—6	—	[56]
Ru	ZSM	$RuCl_2$	SiO_2 sol	TPABr	96	5—6	—	[56]
Ag	ZSM	$Ag(CH_3COO)$	SiO_2 sol	TPABr	96	5—6	—	[56]
Pt	ZSM	H_2PtCl_6	sol, soluble glass	TPABr, TEABr	96	5—6	—	[56]
Hg	ZSM	$HgCl_2$	SiO_2 (colloidal)	TPABr	96	5—6	—	[56]

Notation: TMOS = tetramethyl orthosilicate, TEBr = tetraethyltitanyl.

the group 1 cations contained in the initial silica sol are not entrained by the solid phase on crystallisation; the solid product obtained after filtration, washing, and the elimination of cations contains 3–20 times less of M^{n+} than the amount introduced into the initial silica sol. A mainly amorphous phase is obtained in the presence of Tl^{3+} and Sn^{2+}.

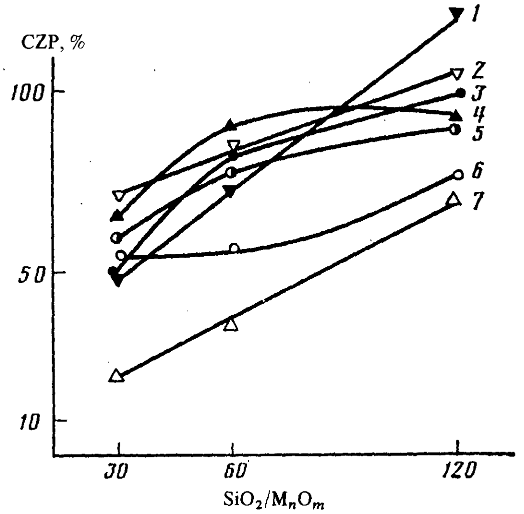


Figure 3. The content of the type ZSM-11 type zeolite phase in the final crystallisation product as a function of the concentration of the added cation in the initial silica sol: *1*) Ga; *2*) Fe; 3) Cr; 4) Mn; 5) Sb; 6) Eu; 7) In.[133]

Table 7. The Si/M^{n+} ratios (mole fractions) in the "decationated" products of the crystallisation of silica gel with the initial ratio $Si/M^+ = 60$ (crystallisation temperature 150 °C).[137]

Cation	Si/M^{n+}	CZP, %	Cation	Si/M^{n+}	CZP, %
Mo^{6+}	700	100	Ga^{3+}	50	125*
Se^{6+}	1000	100	Al^{3+}	70	100
Zn^{4+}	1000	100	B^{3+}	67	100
Ti^{4+}	480	100	Pb^{2+}	150	50
Tl^{3+}	750	70	Sn^{2+}	280	80
Nd^{3+}	700	100	Mn^{2+}	119	100
Eu^{3+}	1300	70	Zn^{2+}	119	100
In^{3+}	330	80	Co^{2+}	27	100
Fe^{3+}	95	100	Cu^{2+}	73	80
Cr^{3+}	56	95	Be^{2+}	36	100

*The content of the zeolite phase of the ZSM-11 type was considered in relation to a standard, for which silicalite was used.

Six-membered coordination by oxygen is stable for group 2 cations (Table 1). Only traces of these cations have been detected in the solid products of the crystallisation of mixtures containing Ti^{4+}, Mn^{2+}, Zr^{4+}, and Mo^{6+} (Table 7).[137] For systems with the Fe^{3+}, Cr^{3+}, Cu^{2+}, Co^{2+}, Ga^{3+}, B^{3+}, Be^{2+} cations, the ratios Si/M^{n+} in the initial gel and its solid crystallisation product are similar. In these systems, the presence of M^{n+} does not prevent the crystallisation of silica sol and the M^{n+} cations are mostly occluded by the crystalline phase formed. The probability of occlusion depends on the size of the cation. Indeed the cations enumerated have the smallest values of ρ among the group 2 cations.

Regardless of the value of ρ, cations with the 4+, 5+, and 6+ charges are not retained by the silicate in any of the groups. Thus the Se^{6+}, Pt^{4+}, Mo^{6+}, and Zr^{4+} cations are present in the crystalline product in trace amounts, which are much smaller than in the initial silica sol. When the alkalinity of the system is the same as under conditions where the silicate crystallises, the cations forming part of the composition of the anion $[NaM_nO_m]^-$ are probably present in a dissolved state.

A high degree of crystallinity of the solid products and similar Si^{4+}/M^{n+} ratios in the initial mixture and in the crystalline phase have been observed for systems with group 3 and 4 cations.[137] Mixtures containing the highly charged V^{4+} and Se^{6+} cations, which are removed from the solid deposit already in the filtration and washing stages, constitute an exception in this instance. Owing to the high alkalinity of the system, vanadate and selenate ions are probably formed and remain in the liquid phase on crystallisation. The presence of compounds containing V^{4+} and Se^{6+} for Si^{4+}/M^{n+} ratios ranging from 15 to 30 hinders the zeolite formation process.[132]

IV. THE STATE OF THE MULTICHARGED CATIONS IN SILICATES WITH THE ZEOLITE STRUCTURE

The state of the multicharged M^{n+} ions in the product of the crystallisation of the $SiO_2–M_nO_m–H_2O$ system can be various and depends both on the composition of the initial mixture and on the nature of M^{n+}. Thus, apart from the fixation of M^{n+} in the silicon–oxygen skeleton in positions isomorphous with Si^{4+}, there is a possibility of occlusion of M^{n+} in salts or oxides within silicate channels or on the outer surface of the crystals and also of their localisation near groups incorporating oxygen ions with an uncompensated charge (in cationic positions). Various methods have been used to investigate the state of the M^{n+} ions: (1) X-ray diffraction (the incorporation of M^{n+} in the skeleton is inferred from the change in the crystal lattice parameters[50,51,54,58–61,64,71]); (2) high-resolution NMR which makes it possible to determine the symmetry of the coordination environment and the composition of the second coordination sphere of the silicon atoms;[132,133,135–138] (3) EPR and Mössbauer spectroscopy (when paramagnetic cations are introduced into the composition of the silicates[131,134,139]). The principal results of these studies are considered below.

1. The State of Mn^{2+}

The state of the Mn^{2+} cations in the elementosilicates obtained from silica gel with added $MnCl_2$ has been investigated by EPR.[134] EPR spectra with an isotropic *g*-factor of ~2.00 have been recorded for all the manganese-containing silicates with the structure of the type ZSM zeolite. The spectrum of the Mn^{2+}-containing elementosilicate at 77 K (Fig.4) can be represented by a superposition of two signals with a Lorentzian shape and a width of 1250 and 450 G and a 6-component spectrum in which the splitting between the third and fourth components is 93 G. Their relative contributions to the overall intensity are 91, 8.5, and 0.5% respectively. The Mn^{2+} cations, to which the signals of the first two types correspond, are probably present in a state with a weak interaction. In the EPR spectra of cations of the third type the splitting between the hyperfine structure components is 90–98 G; the splitting increases as the temperature of the recording is reduced and on passing to the Q-range. This spectrum can be attributed to Mn^{2+} cations in an octahedral oxygen environment. In this case, as in type X and Y zeolites,[138] the width of the EPR line is determined by the relaxation due to the periodic modulation of the crystal field caused by the distortion of the solvation shell of the ion and the anisotropic movement of the solvated ion.

The Mn^{2+} ions responsible for the hyperfine structure (HFS) in the EPR spectrum are apparently not "built into" the zeolite skeleton and are separated from the oxygen atoms of the skeleton by the solvation shell. An additional confirmation of this conclusion has been obtained in a study of the EPR spectra of specimens of elementosilicates heated at 500 °C and a pressure of 10^{-5} mmHg for 2 h. Instead of the superposition of several signals, single lines were observed in the EPR spectra of these specimens, whose width depended on the amounts of water and oxygen adsorbed after the activation of the specimen. On the basis of the form of the EPR spectra, one may claim that there are no Mn^{2+} ions in the test specimen in a tetrahedral environment of oxygen atoms. We may note that the EPR method by no means permits the detection of all the manganese ions introduced into the specimens.[134]

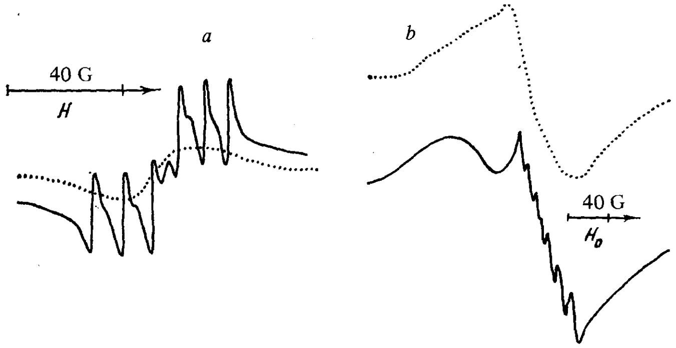


Figure 4. The EPR spectrum of the Mn^{2+} cations of a manganese-containing silicate recorded in the X-range (a) and Q-range (b) at 20 °C (dashed lines) and –110 °C (continuous lines).[134]

2. The State of Cr^{3+}

The EPR spectra of specimens of elementosilicates containing chromium exhibit a symmetrical signal with $g = 1.98$ and $\Delta H = 600$ G,[131] which may be assigned to the disperse chromium hydroxide $[Cr(OH)_3.nH_2O]$. After heating the specimens at 300 °C and above, the intensity of this signal diminishes together with an increase in its width. This may be caused by the dehydration of the hydroxide with formation of the antiferromagnetic Cr_2O_3, or, which is most probable, the oxidation of the Cr^{3+} ions in the chromium oxide particles. The latter hypothesis has been confirmed by the appearance of a signal due to the Cr^{5+} ions, whose intensity increases with increase of the heat treatment temperature. The distribution of the chromium ions detected by EPR on the surface of silicate crystals is indicated by the change in the spectra of the Cr^{5+} ions following the adsorption of pyridine.

3. The State of Cu^{2+}

Signals of mainly two types (I and II) are observed in the EPR spectra of specimens of elementosilicates[131,139] synthesised in the presence of Cu^{2+} ions:

$$g_{\parallel}^{\mathrm{I}}=2.30 \quad A_{\parallel}^{\mathrm{I}}=160\ \mathrm{G} \quad g_{\perp}^{\mathrm{I}}=2.055 \quad A_{\perp}^{\mathrm{I}}=25\ \mathrm{G}$$
$$g_{\parallel}^{\mathrm{II}}=2.32 \quad A_{\parallel}^{\mathrm{II}}=157\ \mathrm{G} \quad g_{\perp}^{\mathrm{II}}=2.058 \quad A_{\perp}^{\mathrm{II}}=26.5\ \mathrm{G}$$

The parameters of these signals correspond to Cu^{2+} ions fixed in an octahedral oxygen environment. The difference between the parameters of the ions of types I and II is probably determined by the existence of tetrahedral distortions for the type II Cu^{2+} ions. After the specimens have been heated at 250 °C and above, the intensity of the EPR signals of the Cu^{2+} ions is found to increase. It is noteworthy that some of the detected Cu^{2+} ions are inaccessible to the adsorbed molecules, which is indicated by the absence of changes in the EPR spectrum after the adsorption of pyridine. The copper ions interacting with pyridine give rise to an EPR spectrum with the $g_{\parallel} = 2.26$, $A_{\parallel} = 1.86$ G and $g_{\perp} = 2.08$, $A_{\perp} = 40$ G signals, which is due to the formation of pyridinates.[131]

Overall, the hydrothermal synthesis of elementosilicates from silica gel containing copper compounds results in the stabilisation of the bulk of the copper (~90%) in a state undetectable by EPR, probably in the form of an oxide phase. A small proportion of the copper (~10%) is stabilised in the form of isolated ions and, after treatment with thionyl, in a specific form with antiferrodistortion order.[139]

The crystal lattice parameters of the copper-containing zeolite do not differ from those of the unmodified zeolite, which provides additional grounds for the assumption that the isomorphous substitution of silicon atoms by copper atoms with tetrahedral coordination does not occur. It is more likely that the copper cations are localised in the channels of the zeolite structure and that the exchange interaction between them takes place via silicon–oxygen bridges or via oxygen atoms which do not belong to the zeolite skeleton.

4. The State of V^{4+}

The character of the X-ray diffraction patterns of specimens of vanadium-containing elementosilicates shows that the systems synthesised are mixtures of three phases: silicalite (crystalline SiO_2 with the zeolite structure), α-quartz, and an admixture of amorphous SiO_2. With increase in the amount of VO_2^- introduced into the initial sol, the content of the crystalline silicate phase in the specimen diminishes, as a result of which the actual SiO_2/V_2O_5 ratio in the solid phase is smaller by a factor of 4–10 than in the initial gel.

Low values of the HFS constant for the parallel orientation as well as the dependence of the character of the EPR spectrum on the temperature of the measurement are to be expected for a V^{4+} ion in a tetrahedral coordination.[140]

The EPR spectrum of vanadium-containing silicates obtained by hydrothermal synthesis is characteristic of V^{4+} ions in an octahedral coordination with tetragonal distortion ($g_{\parallel} = 1.93$, $A_{\parallel} = 1.95$ G and $g_{\perp} = 1.96$, $A_{\perp} = 56$ G) in the isolated (as part of the composition of VO_2^-) and exchange-linked states. Since the intensity of the EPR signal of V^{4+} proved to be many times smaller than might have been expected from chemical analysis, it was concluded that the main bulk of the V^{4+} ions present in the silicate are bound by a strong exchange interaction and are present in the composition of polymers. The EPR spectrum of the V^{4+} ions in this state has not been observed.[141]

Thus there are no grounds for the assumption that the V^{4+} cation is "built into" the silicon–oxygen skeleton in tetrahedral positions in the course of the hydrothermal synthesis of silicates with a zeolite structure.

5. The State of Fe^{3+}

The incorporation of Fe^{3+} ions into the composition of type A, X, and Y zeolites in the hydrothermal synthesis of the latter has been frequently established.[142–147] The source of Fe^{3+} consists of the admixture of iron compounds present in the components of the initial mixture. Thus it has been shown[142] that 0.01% of Fe^{3+} cations are occluded in type Y zeolites obtained by hydrothermal synthesis. Three signals, with $g = 4.27$, 2.4, and 2.0, have been observed in the EPR spectra. The signal with $g = 2.4$, whose width was 1600 G and which diminished with increase of temperature, was assigned to magnetite Fe_3O_4, which has ferromagnetic properties. The Curie point, determined from the magnetic susceptibility, was at 572 °C and was attributed to the highly defective nature of the phase produced. The EPR spectrum of Fe^{3+} occluded in the zeolite NH_4Y and mordenite was found to contain three signals:[143] with $g = 4.3$ (narrow), 2.3, and 2.0 (both broad). The first was assigned to Fe^{3+} fixed in a tetrahedral oxygen environment with pronounced orthorhombic distortion. The signal at $g = 2.0$ was assigned to all the cations in the octahedral environment incorporating three oxygen atoms and three OH groups at cationic sites.

The EPR spectra of the Fe^{3+} ions forming part of the composition of a type Y zeolite[144–146] have been interpreted in the same way: the signals with $g = 2.2–2.3$ were explained by the presence of an amorphous oxide phase[143] and an occluded salt,[145] in which the Fe^{3+} cations are in a state with strong exchange interaction. The fraction of Fe^{3+} cations in a tetrahedral environment ($g = 4.3$) was ~4% of the total Fe_3O_4 content in the zeolite. The part of Fe^{3+} forming part of the composition of the phase giving rise to the signal with $g = 2.2–2.3$ was most readily extracted.

A zeolite of the ZSM-5 type, in which the Fe^{3+} cations were introduced before the hydrothermal crystallisation of silica gel, has been synthesised[146] in the presence of hexamethylenetetramine. The general character of the EPR spectrum resembles that described above.[142–145] After the reductive treatment of the specimen, the intensity of the signal with $g = 2.02$ diminished markedly, while the intensity of that with $g = 4.28$ remained almost unchanged.

A characteristic signal with $g = 4.3$ (Fig.5*a*), which can be assigned to isolated Fe^{3+} ions, was observed[131] in the EPR spectra of iron-containing elementosilicates with the ZSM structure. The transitions near $g = 4.3$ in the low-field part of the spectrum refer to Fe^{3+} ions whose ligand environment is appreciably distorted (type I). The main transitions noted in Fig.5 can be assigned to Fe^{3+} ions stabilised in a weakly distorted octahedral environment (type II) ($D, E \leq h\nu$). Analogous spectra have been observed for Fe^{3+} ions in the hexa-aquo-complexes formed on dissolution of iron salts in water at low concentrations. The absence of a significant temperature dependence of the EPR of type II Fe^{3+} ions also indicates the fixation of the iron cations predominantly in the form of isolated ions. A symmetrical line in the vicinity of $g = 2.00$ (type III), characteristic of exchange-bound Fe^{3+} ions, can be observed in the EPR spectrum of the specimens obtained at 200 °C.

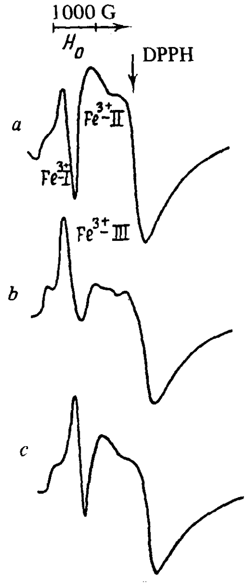


Figure 5. The EPR spectrum of the Fe^{3+} cations of an iron-containing silicate: *a*) initial specimen; *b*) after dehydration at 400 °C; *c*) after the adsorption of pyridine on the specimen and subsequent dehydration at 400 °C.[131]

The assignment of the signal with $g = 4.23$ in the Fe^{3+} EPR spectra to Fe^{3+} ions in a tetrahedral coordination does not alone justify the claim that the corresponding Fe^{3+} ions are fixed in the silicon–oxygen skeleton at sites isomorphous with those of Si^{4+}. Indeed the iron oxide compounds can incorporate Fe^{2+} and Fe^{3+} cations fixed in tetrahedral cavities.[140] Some evidence for the view that the Fe^{3+} cation giving rise to the EPR signal with $g = 4.23–4.3$ enters into the composition of the silicon–oxygen skeleton of a type ZSM zeolite has been obtained.[147]

The intensity of the signal with $g = 4.27$ in the EPR spectrum of the products of crystallisation of the $Na_2O.nFe_2O_3.SiO_2.mH_2O$ mixture increased almost in proportion to the content of the zeolite phase (Fig.6), but diminished after ion exchange. On the other hand, the intensity of the signal with $g = 2.0$ was independent of the degree of crystallinity of the specimen but increased with increasing Fe_2O_3 content for the well crystallised specimens. In the studies enumerated above, it was shown that the intensity of the signal of the type I ions is very low. In one study[145] it corresponded to 4% of the total amount of the Fe_2O_3 present in the type Y zeolite. In another study[147] the signal intensity ratio $I_{4.27}/I_{2.0}$ was 20–30.

Thus the literature data permit the conclusion that a small proportion of Fe^{3+} ions are built into the silicon–oxygen skeleton of the elementosilicate in the course of hydrothermal synthesis; most of the ions remain in the iron oxide phase or in cationic sites. These data indicate the possibility of the formation of the $[Si(OFe)_n]^{n-}Fe^{3+}$ groups in the skeleton.

After the removal of cations by acid or NH_4OH solutions, there is a possibility of the rupture of both Si–O–Fe–O–Si and Si–O–Al–O–Si linkages as a result of hydrolysis.

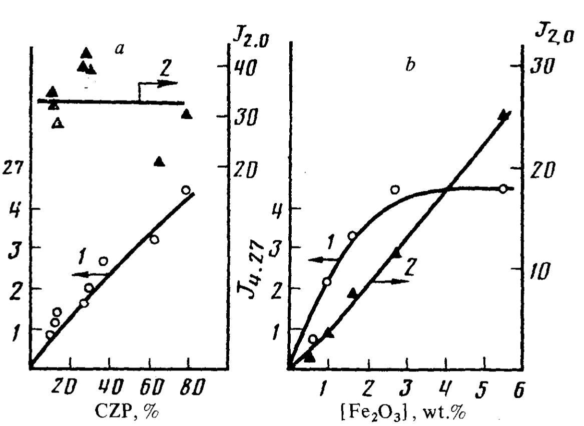


Figure 6. The relative intensities of the EPR signals of the Fe^{3+} cations with $g = 4.27$ (curves *1*) and $g = 2.0$ (curves 2) for a silicate occluding Fe^{3+} ions during hydrothermal treatment as a function of the content of the crystalline phase (*a*) and the content of Fe_2O_3 in the crystallisation product (*b*).[137]

The state of Fe^{3+} at various sites in the silicon–oxygen skeleton of faujasite[148] for Si/Al = 1 has been calculated by the semiempirical LCAO-MO SCF method in the CNDO/2 valence approximation. The authors[148] concluded that the Fe^{3+} cations must be bound to the oxygen atoms in the zeolite skeleton by strong donor–acceptor bonds whose strength is comparable to that of the bonds involving Al^{3+}. Comparison of the charge density and Wiberg indices of the $FeSi_5O_6.(OH)_{12}Na$ and $AlSi_5O_6(OH)_{12}Na$ clusters formed on isomorphous substitution of Si^{4+} in the six-membered silicon–oxygen ring showed that the Al^{3+} and Fe^{3+} ions have identical effects on the properties of the skeleton; the Fe–O bond is stronger than the Al–O bond.

6. The State of Be^{2+}

The isomorphous substitution of the atoms of the silicate skeleton by Be^{2+} ions has been observed in natural minerals: in helvin $Mn_4Be_3O_{12}S$, whose structure is similar to that of sodalite $Na_4Al_3Si_3O_{12}Cl$, with a three-dimensional skeleton formed by the linkage of silicon–oxygen tetrahedra, and in tugtupite,[149] where the isomorphous substitution is of the type $2Al^{3+} \rightleftharpoons Be^{2+}Si^{4+}$. Beryllosilicates with the analcime structure have been synthesised[150,151] at 150–400 °C in the course of 1–3 weeks from gels having the composition $NaBe_{1.5}Si_2O_6$ and $Na_3Be_{1.5}.Si_{4.5}O_{12}.NaCl$. The formula $Na_{16}Be_8Si_{40}O_{96}(H_2O)_{16}$ has been proposed for the final product. Its derivatograms showed an exothermic peak at 150–500 °C. The authors attributed its appearance to the removal of zeolitic water.

It has been noted[151] that the size of the unit cell and the refractive index of the products formed decrease linearly with increasing degree of isomorphous substitution $2Al^{3+} \rightleftharpoons Be^{2+}Si^{4+}$. These facts are regarded as proof of the occurrence of isomorphous substitution. Thus the unit cell of $Na_3Al_{2x}Be_{1.5-x}Si_{5-x}O_{13(4-2x)}$, synthesised under condtions with $0 \leq x \leq 1.5$, varies from 13.72 Å for the zeolite without Be^{2+} cations to 13.36 for beryllosilicate, while the refractive index varies correspondingly from 1.48 to 1.519.

The state of the Be^{2+} cations in the solid state can be investigated by NMR. The interpretation of the ^9Be NMR spectra is made difficult by the high sensitivity of the spin–lattice relaxation, which requires an exact determination of the strengths of the pulse for each specimen analysed, and by the low intensity of the signal obtained. The $[Be(H_2O)_4]^{2+}$ ion gives rise to a narrow resonance line at 50 and 1000 Hz, which indicates a symmetrical tetrahedral environment with quadrupolar interaction whose extent is close to zero.

It has been concluded[152] that a Be^{2+} ion in a tetrahedral environment gives rise to an NMR signal in a stronger field than the same ion in the tricoordinate state. A Be^{2+} ion in a three-membered environment gives rise to a ^9Be NMR signal with a chemical shift δ, relative to $[Be(H_2O)_4]^{2+}(NO_3)_2$, ranging from −21 to −11 p.p.m., while the same ion in a tetrahedral environment gives rise to a signal ranging from −12 to +1 p.p.m. The substitution of the negative ions of the environment by ions with a higher negative charge leads to a downfield shift of the signal. The introduction of strong bases into the environment of Be^{2+} causes an upfield shift of the signal. For example, the substitution of CH_3^- by Cl^- in the first coordination sphere of the Be^{2+} cation results in a shift of the NMR line from −4.2 to −5.5 p.p.m. The ^9Be NMR spectra of $BeCl_2$ in dimethyl sulphoxide, diethyl ether, and ammonia have $\delta = -5.5$, −3.1, and −1.7 p.p.m. respectively.

The state of Be^{2+} in beryllosilicates with the zeolite ZSM structure was investigated by the ^9Be NMR method for the first time by Ione and co-workers.[132,133,137] The spectra consisted of a single signal, whose chemical shift relative to that of ^9Be in the spectrum of sodium beryllate was −5.8 p.p.m. (Fig. 7*a*). The character of the spectrum differs also from that of beryllium oxide. The intensity of the ^9Be NMR signal is proportional to the amount of beryllium determined by chemical analysis. Comparison of the ^9Be NMR signal intensity and the Be^{2+} content determined by chemical analysis showed that most of the Be^{2+} ions in the silicate synthesised are fixed in the crystalline silicon–oxygen skeleton.[153]

7. The State of P^{5+}

Like Si^{4+}, the P^{5+} cation can have a tetrahedral oxygen environment and can form a three-dimensional phosphorus–oxygen skeleton. Bearing in mind the similarity of the radii of the above cations, one may expect the occurrence of the isomorphous substitution $PO_4^{3-} \rightleftharpoons SiO_4^{4-}$. In nature, this phenomenon has been observed in the mineral viséite, which is a structural analogue of analcime.[24]

Phosphorus-containing crystalline silicate with the analcime, chabazite, phillipsite-harmotome, and type A, L, and B(P) zeolite structures, containing 5–25% [of phosphorus? (Ed.of Translation)], have been synthesised.[154] It has been established that the lattice constant diminishes with increasing P_2O_5 content in the type Y zeolite (thus $a = 12.249$ Å in the presence of 5.2% of P_2O_5 and $a = 12.232$ Å in the presence of 10% of P_2O_5). The increase of the cell parameter is caused by the fact that the length of the P–O bond (1.54 Å) is smaller than those of the Si–O (1.61 Å) and Al–O (1.75 Å) bonds. With increase of the P_2O_5 content in the type A zeolite, the intensity of the refraction also changes almost linearly. These data enabled the authors[154] to conclude that the $Si^{4+} \rightleftharpoons P^{5+}$ isomorphism occurs in the type A zeolite synthesised.

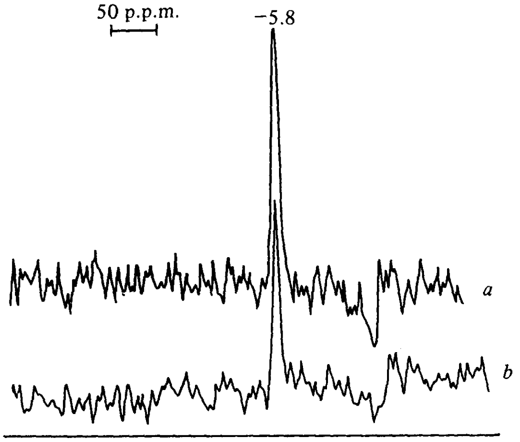
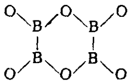


Figure 7. The ^9Be NMR spectrum of crystalline beryllosilicates; SiO_2/BeO_2 ratio in initial hydrogel: *a*) 60; *b*) 30.[137]

8. The State of B^{3+}

It has been established that B^{3+} cations in a tetrahedral coordination are present in the BF_4^-, BH_4^-, $[HB(OR)_3]^-$, and $[B(C_6H_5)_4]^-$ anions. In compounds with oxygen, boron forms either a planar structural BO_3^- unit with angles of 120° between the bonds or boron–oxygen tetrahedra (in glasses). In solutions, $B(OH)_3$ polymerises with formation of cyclic polymers, whose presence has been established also in crystalline borates. The latter include both BO_3^- groups and BO_4^- groups and consist of six-membered rings of the type



This has been demonstrated by ^{11}B NMR.

The boron phosphate BPO_4, obtained by the interaction of boric and phosphoric acids, includes a tetracoordinate boron atom; the phosphate contains B–O–P linkages.[140]

Borosilicates and aluminoborates with zeolite structures have been synthesised in many studies. The substitution of Si^{4+} by B^{3+} cations in the zeolite skeleton was not demonstrated by Barrer and Marchilly.[155] It has been suggested[156] that boron cations are occluded in the zeolite cavities in the compound $NaBO_2$ or $NaB(OH)_4$. These conclusions conflict with data[157] according to which all the unit cell parameters of borosilicates decrease almost linearly with increase of their B_2O_3 content (Table 8). The B_2O_3 content was determined from the amount of the carbon-containing precursors of borosilicates. Simultaneously with increase of the ratio B/(B + Si), a transition from the monoclinic to the orthorhombic system was observed.

The state of the B^{3+} ions in a silicate isostructural with the zeolite ZSM-11 has been studied systematically as a function of the conditions of their synthesis;[132,133,135,136] the elementosilicates were synthesised by the method of Ione et al.[130] Two lines were observed in the ^{11}B NMR spectra of borosilicates—a symmetrical narrow line with a width of ~1.7 kHz and a chemical shift of −23.3 p.p.m. (signal I) and a broad line with $\delta = -17 - 64$ p.p.m. (signal II).[135]

Table 8. The unit cell parameters as a function of the ratio B/(B + Si) in borosilicates with the zeolite structure.[157]

B/(B + Si)	*a*, Å	*b*, Å	*c*, Å	*d*, Å	*v*, Å^3
0	20.117	19.874	13.371	90.62	5345.5
0,007	20.087	19,852	13.364	90.46	5329.3
0.016	20.050	19,822	13.372	90.00	5314,3
0.022	20.022	19.816	13,340	90.00	5292.6
0.041	20.002	19.805	13,334	90.90	5282.1
0.049	19.974	19.774	13.306	90.90	5255.9
0.109	19.934	19,716	13,269	90.00	5215,0

The NMR spectra of the glasses usually show two types of lines due to the boron atoms in different coordination environments.[158] At a frequency of 30 MHz, a second-order quadrupolar splitting of ~15 kHz occurs for boron atoms in ternary coordination, which corresponds to a quadrupolar interaction constant of ~2 MHz. For tetracoordinate boron atoms, the quadrupolar interaction constant is much smaller. As a result of the latter, the spectrum of boron in a tetrahedral oxygen environment does not exhibit second-order splitting even at low frequencies; the line due to boron atoms in a tetrahedral environment is comparatively narrow and symmetrical. As a result of this, the narrow symmetrical line I, observed in the NMR spectra of borosilicates, can be assigned to boron atoms in a tetrahedral oxygen environment.

With increase of the ratio OH/SiO_2 in the initial borosilica sol, the chemical shift of the ^{11}B NMR signal in the spectra of the resulting borosilicates did not change, but the intensity of the main spectral line with $\delta = -23.3$ p.p.m. (signal I)[135] diminished. The degrees of crystallinity of the corresponding borosilicate change in the same sequence (NaB-0.1 > NaB-0.2 > NaB-0.3) with virtually identical total B_2O_3 contents in these substances (Table 9). The increase of the crystallisation time from 48 to 144 h (NaB-0.1 specimens) led to a comparatively small decrease of the intensity of signal I without change in the chemical shift and line width. The degree of crystallinity of the corresponding specimens (NaB-0.1 series) hardly changed under these conditions, but their B_2O_3 content diminished somewhat. With decrease of the B_2O_3 concentration in the specimens (from 4 to 0.7%), the intensity of signal I in the ^{11}B NMR spectra also fell.

Comparison of all the data enabled the authors[135,137] to postulate that signal I with $\delta = -23.3$ p.p.m. corresponds to boron atoms fixed in the crystalline part of the borosilicate synthesised as part of the composition of the silicate skeleton. Significant differences have been observed between the ^{11}B NMR spectra of freshly prepared specimens and the same specimens after a test in the catalytic conversion of methanol and after subsequent regeneration by annealing in air at 520 °C. The intensity of signal I in the

^{11}B NMR spectra decreases sharply, while the intensity of the broad band increases. In the course of the treatment of borosilicates at elevated temperatures in the presence of water vapour, the Si–O–B linkages are probably hydrolysed with the accompanying displacement of the B^{3+} cations from sites with a tetrahedral oxygen environment.[137]

Table 9. The influence of the ratio OH/SiO_2 in the initial mixture and of the crystallisation time τ on the content of the borosilicate phase isostructural with the ZSM-11 zeolite (crystallisation temperature 150 °C, SiO_2/B_2O_3 = 60).[135]

Specimen	OH/SiO_2	τ, h	$[B_2O_3]$, wt.%	S, m^2g^{-1}	CZP, %	I_{rel}
NaB-0.1	0.1	48	1.6	570	90	1.0
	0.1	78	1.5	580	100	0.9
	0.1	120	1.4	530	95	0.8
	0.1	144	1.2	540	90	0.7
NaB-0,2	0.2	48	1.8	170	30	0.4
NaB-0.3	0.2	120	1.1	120	16	—
	0.3	48	2.1	180	20	0.2

Notation: $[B_2O_3]$ = B_2O_3 concentration in the silicate and I_{rel} = relative intensity of signal I in the ^{11}B NMR spectrum.

9. The State of Ga^{3+}

The structure and properties of the oxygen-containing Ga^{3+} compounds are similar to those of aluminium oxides.[140] Gallium trioxide ε-Ga_2O_3 as well as gallate ions contain both tetracoordinate and octacoordinate Ga^{3+} ions.

Chabazite and phillipsite have been synthesised[159] in the presence of Ga^{3+} cations, but evidence for the isomorphous substitution of Si^{4+} by Ga^{3+} was not published. A type X zeolite has been synthesised[160] in the presence of Ga^{3+} cations and a change in the unit cell parameters was observed. Sodalite with the ratio $SiO_2/(Ga_2O_3 + Al_2O_3)$ = 1.28 and Na-GaX (1.14), Na-GaX (1.42), and Na-GaY (2.17) faujasites have been obtained[16] by the hydrothermal method. The Al_2O_3 content in these silicates was ~1% of the amount of Ga_2O_3 introduced. The state of the Si^{4+} and Ga^{3+} ions in the zeolite was investigated by ^{29}Si and ^{71}Ga NMR respectively and it was shown that the intensity of the NMR signal depends on the Si/Ga_2O_3 ratio, which was determined by chemical analysis.[160,161]

Comparison of the chemical shifts of the ^{29}Si NMR signals of zeolites having the silicon–oxygen composition and their gallium analogues[160,161] showed that the introduction of Ga instead of Al diminishes somewhat the shift of the peaks corresponding to the Si–$(OM)_n$ groups, where M = Ga or Al. The intensity of the peaks corresponding to the Si–OM and Si–$(OM)_2$ groups in the case of Ga-sodalite is smaller than for the Al–Ga-zeolites.

A ^{29}Si NMR signal, whose chemical shift is also smaller than in the case of the aluminium-containing analogues, is characteristic of type X and Y gallium-containing zeolites. The relative intensities of the peaks in the ^{29}Si NMR spectra of Ga- and Al-faujasites are similar, which indicates the identical character of the distribution of the corresponding elements in both cases.

The ^{71}Ga NMR signal of the zeolite Ga-Y, obtained by Thomas et al.[161], is broad and its chemical shift relative to $Ga(NO_3)_3$ is −182.5 p.p.m. The ^{29}Si NMR signal with $\delta = -75.5$ p.p.m. has been assigned to Si–$(OGa)_4$ and that with $\delta = -81.5$ p.p.m. has been assigned to Si–$(OGa)_3$. The ^{29}Si NMR spectrum of Ga-thomsonite includes signals with $\delta = -82.9$ and −83.5 p.p.m. The MAS ^{71}Ga NMR spectrum has been measured[132,137] for a gallosilicate with the ZSM-11 structure, obtained by the method of Ione et al.[130], and was found to contain one broad band with a chemical shift relative to $Ga(NO_3)_3$ of 154–155 p.p.m. (Fig.8).

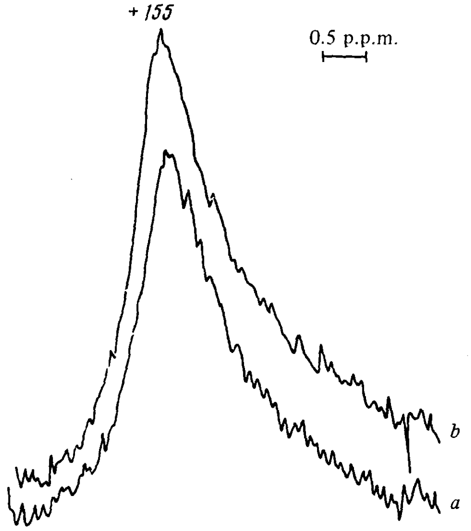


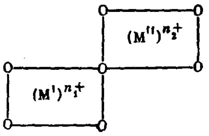
Figure 8. The ^{71}Ga NMR spectrum of crystalline gallosilicates with the ZSM-11 structure; SiO_2/Ga_2O_3 ratio in the initial silica sol: *a*) 60; *b*) 30.[137]

The set of data obtained by the ^{29}Si and ^{71}Ga methods justifies the assumption that the degree of isomorphous substitution and the character of the distribution of the Ga^{3+} ions in the silicon–oxygen skeleton are similar to the corresponding parameters for Al^{3+}.

Thus, depending on the type of the cation and the conditions in the hydrothermal treatment of the initial gel in the thermochemical treatment of the finished products, the modifying element M^{n+} can be fixed (1) in the composition of the individual (oxide or hydroxide) phase within cavities or outside the silicate crystals with the corresponding octahedral (for transition metal cations) and ternary (for boron) coordination, (2) in cationic sites in the form of species neutralising the negative charge of the skeleton, and (3) in the silicon–oxygen skeleton with a tetrahedral symmetry of the environment comprising oxygen atoms at sites isomorphous with respect to those of the Si^{4+} cations. The catalytic properties of the silicates should depend significantly on the state and the degree of coordination of the M^{n+} cations. Thus in the first case the individual phase can behave under the reaction conditions as an inert additive or can exhibit catalytic activity in oxidation-reduction reactions. The conversion of methanol on silicates with such additives can proceed with decomposition to CO and H_2. The M^{n+} cations fixed in silicates in accordance with types 2 and 3 should influence the acid–base properties of the latter.

V. CATALYTIC PROPERTIES

Crystalline silicates with zeolite structures (elementosilicates) are binary oxide systems like zeolites themselves. According to general ideas developed by Pauling[1] and Tanabe,[1,2] the acid–base properties of the binary oxides are determined by the incomplete compensation of the charges of the oxygen ions in polyhedra differing in the charges of their cations. Thus an uncompensated charge Z is generated on the oxygen atoms of the two polyhedra $M'O_4$ and $M''O_4$



with $n_1 \neq n_2$. According to Pauling's second rule,[162] the charge of the anion must be equal to the sum of the electrostatic forces of the bonds between the anion and the surrounding cations. The electrostatic strength of the bond is defined by Pauling as the ratio of the charge of the cation (en_i) to its coordination number (c). Hence the following formula is obtained for oxygen atoms in binary oxides:

$$Z=\frac{en_1}{c}+\frac{en_2}{c}.$$

The formation of a proton-donating centre on a polyhedron with an excess charge takes place (a) on substitution of the cation, compensating for the excess charge of the polyhedron, by a proton; for example, we have for silicates with a tetrahedral coordination of the cation

$$[(OSi)_n(OM)_{4-n}]^{(4-n)-}\cdot Na^+ \xrightarrow[-Na^+]{+H^+} [(OSi)_n(OM)_{4-n}]^{(4-n)-}\cdot H^+.$$

(b) In the heterolytic dissociation of water molecules in the field of the oxygen atoms of the polyhedron and the cation compensating for the charge:

$$[(SiO)_n(MO)_{4-n}]^{(4-n)-}\cdot H^+ + \ldots OH^- — M^{n+}.$$

The energy of the $\rangle$O...H bond in the $\overset{M}{\underset{Si}{\rangle}}$O...H group should diminish in a series of polyhedra with the cations $M^+ > M^{2+} > M^{3+}$, because the excess charge on the oxygen atoms decreases in the same sequence. For this reason, if the mobility of the proton in the $[(SiO)_n(MO)_{4-n}]^{(4-n)-}H^+$ group is adopted as a measure of its proton-donating activity, then the mobility should decrease in the sequence $M^{3+} > M^{2+} > M^+$.

Thus the proton-donating activity of silicates incorporating triply charged ions at sites isomorphous with those of Si^{4+} should be greater in the presence of doubly and singly charged cations.

Evidently the strength of the acid centres of silicates incorporating M^{n+} cations with identical charges should depend on the radius of the cations. The strength of the acid centres has been compared[163] with the difference between the electrostatic potentials (ΔV) of the BO_x and AO_y polyhedra at the sites of the B → A substitution:

$$\Delta V=\sum_i (q_i/r_i)_{BO}-\sum_i (q_i/r_i)_{AO},$$

where q_i is the charge of the ion at a distance r_i from the site A in the $BO_x.nAO_y$ matrix.

If one begins with the fact that the degree of polarisation of the O–H bond in the $[(SiO)_n(OM)_{4-n}]^{(4-n)-}H^+$ group depends on the electrostatic potential e/r in the field of the cation M and if the M–O bond length in the silicate is the same as in the oxide of M, then the acidity of the OH group in silicates incorporating triply charged cations should diminish in the sequence $B^{3+} > Al^{3+} > Ga^{3+} > Fe^{3+} > In^{3+}$ with decrease of e/r for these cations. However, this approximation has little predictive power, because the assumption of the equality of the M–O bond lengths in the silicate and the oxide has not been confirmed experimentally.

No studies have been published hitherto in which the variation of the strength of the acid centres of silicates was estimated as a function of the nature of the cation M^{n+} substituting Si^{4+} isomorphously in the silicate skeleton. So far there have been few studies in which the strength of the acid centres of such systems has been determined experimentally. Their comprehensive investigation is only beginning. The ^1H NMR method has been applied[164] in a comparative determination of the proton-donating strength of the OH groups in the zeolite ZSM-5 and borosilicate (H-borolite). The authors based their conclusions on the assumption that the chemical shift of the ^1H NMR signal reflects the degree of shielding of the proton nuclear spin by electrons and can serve as a measure of acidity. The authors observed that the ^1H NMR spectra of the two specimens each contain two signals—with δ = 6 and 2 p.p.m. (ZSM-5) and 3.5 and 2 p.p.m. (H-borolite). The signal at δ = 2 p.p.m. was assigned to the Si–OH groups, that with δ = 3.5 p.p.m. to the Si–O–B groups, and that with δ = 6 p.p.m. to the Si–O(H)–Al groups. The authors[164] concluded that the acidity of the OH group also increases in this sequence.

The catalytic activity of the solid surface is known to depend not only on the strength but also on the concentration of the active centres present on it. It has been established[165] on the basis of the relative intensities of the ^{11}B NMR signals of the boron cations having tetrahedral and ternary coordination in borosilicates with zeolite structures that only 5–10% of the total number of the B^{3+} detected in the specimens by chemical analysis is fixed in the former state.

It has been demonstrated[147] by ^{11}B and ^{71}Ga NMR that not more than 10–20% of the total amount of the elements which were determined by chemical analysis in the hydrothermal crystallisation product are present in a tetrahedral oxygen environment in zeolites with the erionite structure synthesised in the presence of the B^{3+} and Ga^{3+} cations.

Thus the true concentration of the cations substituting isomorphously the silicon atom in the silicon–oxygen skeleton and hence also the number of the catalytically active centres can be much less than the total content of the given element in the silicate. The latter factor hinders the determination of correlations between the nature of the M^{n+} cations fixed at isomorphous sites and the catalytic properties of the silicates. Nevertheless the data considered above show that the hydrothermal synthesis of the sources of SiO_2 in the presence of sources of multicharged M^{n+} cations leads to the formation of silicates with the zeolite structure, whose catalytic properties differ from those of aluminosilicate zeolites.

1. Germanium-containing Elementosilicates

The catalytic properties of the NaGe-X faujasite, synthesised from the Al–Ge gel and having the composition $Na_{75.8}(NH_4)_{20.2}(AlO_2)_{96}(GeO_2)_{96}$ have been investigated[166] in the isomerisation reaction of n-butenes at 150–350 °C. Comparison of the properties of the faujasites based on Al_2O_3–SiO_2 (HX and HY) and Al_2O_3–GeO_2 (HGeX) led to the following findings.

1. For high degrees of ion exchange, significant breakdown of the crystal lattice of the germanosilicate is observed as a consequence of the lower stability of the germanium–oxygen zeolite skeleton compared with that of the silicon–oxygen skeleton having an analogous structure.
2. In the presence of HGeX specimens, the isomerisation of n-butenes proceeds in accordance with a first-order equation without change in the kinetic parameters for 3.5 h, while in the presence of HX and HY the first order of the reaction is maintained only in the first 6 min after the start of the experiment. The catalytic activity of the zeolite HY falls during 1.5 h by a factor of 7, while the activity of HGeX does not change during this period.
3. The activation energy and selectivity of the process are close to those observed for HX and HY when the reaction is carried out in the presence of HGeX.
4. The rate of reaction, referred to a single active centre, and the average acidity of the OH groups diminish with increase of the Si, Ge/Al ratio in the zeolite HGeX. The process proceeds, as for the HY and HX catalysts, with participation of Brønsted acid centres.

2. Boron-containing Elementosilicates

Boron-containing faujasites have been investigated in the cracking of cumene[39] and it has been shown that their catalytic properties resemble those of the Al, Si-faujasites.

Data[55,58] concerning the catalytic properties of boron-containing silicates (borolites) in the synthesis of t-butyl methyl ether (TBME) from methanol and isobutene are of great interest. It has been shown that at 150–170 °C it is possible to attain a high degree of conversion of the initial reactant and that the yield of TBME in the presence of type B, C, and D borolites is 96–99.3%. The borolites proved to be highly selective and stable catalysts of the decomposition of TBME to isobutene and methanol over a wide temperature range; they ensure a selectivity of 99.8% and do not induce the subsequent conversion of isobutene and methanol. In contrast to this, in the presence of aluminosilicate zeolites methanol can be dehydrated with subsequent redistribution of hydrogen in the resulting olefins. The type C borolite acts as a catalyst of the alkylation of benzene by ethylene at 450 °C, a space velocity of 4 h^{-1}, and for the ratio benzene/ethylene = 5.[69,70]

According to the data in Ref.71, borolites are catalytically inactive in the synthesis of hydrocarbons from methanol. Bragin et al.[67] arrived at the opposite conclusion having established that borolites with the zeolite structure exhibit a high activity and selectivity in this reaction. The catalytic properties of borosilicates in the synthesis of hydrocarbons from methanol have been investigated[129–137] as a function of the state of the boron atoms in the silicate skeleton and of the content of the Al^{3+} admixture in them. Under the same conditions, the highest degree of conversion was attained in the presence of boron-containing aluminosilicates with SiO_2/Al_2O_3 ratios of 126 and 220 (Table 10, specimens 1 and 2). The catalytic properties of these specimens are typical for type ZSM zeolites with the same SiO_2/Al_2O_3 ratio. At 380 °C the degree of conversion of methanol is close to 100% and the fraction of C_5 and higher hydrocarbons is 57 to 60% of all the hydrocarbon reaction products and includes 16–27% of aromatic compounds.[136]

The borosilicates in which the Al_2O_3 content is very low (SiO_2/Al_2O_3 > 1000) and the SiO_2/B_2O_3 ratio is 25 and 46 have sharply different catalytic properties from those of aluminosilicates (Table 10): at 380 °C the main reaction product is dimethyl ether and C_2–C_7 olefins. The content of aromatic hydrocarbons in the reaction products is less than 2%.[135] With increase of the reaction temperature from 380° to 500 °C, the content of dimethyl ether in the reaction product falls (from 54 to 56% for specimens with SiO_2/B_2O_3 = 30), while that of aromatic and aliphatic hydrocarbons increases sharply (from 1.2 to 13.6 and from 32.5 to 67.8% respectively). However, after the reaction–regeneration cycle, the selectivity of the action of the catalysts changes: the selectivity diminishes with respect to the higher hydrocarbons and increases with respect to dimethyl ether.

Table 10. The degree of conversion of methanol and the composition of the reaction products in the presence of boron-containing silicates* with the ZSM-11 structure.[36]

Silicate	Chemical composition of silicate			α**, %	Composition of carbon-containing reactions products, %				
	$[Na_2O]$, wt.%	SiO_2/B_2O_3	SiO_2/Al_2O_3		DME***	C_2–C_7 olefins	aromatic hydrocarbons	C_5 and higher fractions	C_1–C_4 fractions
Boroaluminosilicate-1	0.08	37	126	100	traces	—	27.4	57.0	43.0
Boroaluminosilicate-2	0.12	102	220	100	10.2	—	16.2	61.6	28.2
Borosilicate No.3	0.03	25	1000	76	54.3	32.5	1.2	10.4	2.8
Borosilicate No.4	0.05	46	1000	69	79.1	15.6	1.6	4.3	1.0
Borosilicate No.5	0.05	135	1000	42	100.0	0	0	0	0
Silicalite	0.05	—	1500	1—2	100	0	0	0	0

*Reaction temperature 380 °C, contact time (gas phase) 20–30 s, methanol content in mixture 20 vol.%, pressure 1 atm.

**Degree of conversion of methanol.

***Dimethyl ether.

Cyclic compounds were not detected in the reaction products for specimens with SiO_2/B_2O_3 = 135 and silicalite (Table 10). These results show that the high catalytic activity of boron-containing zeolites in reactions involving the synthesis of aliphatic and aromatic hydrocarbons from methanol, observed in some investigations, is due to admixtures of aluminium. Nevertheless, there is a relation between the content of B_2O_3 in borosilicates and the degree of conversion of methanol, which supports the hypothesis that the B^{3+} cations enter into the composition of the active centres. However, as shown above, a considerable proportion of the boron cations are displaced from the silicate skeleton on elimination of cations and in the reaction–regeneration cycles. The boron atoms remaining in the tetrahedral coordination at sites isomorphous with those of silicon (or aluminium) atoms apparently constitute a significant proportion of the entire B_2O_3 introduced.

It has been established in a number of studies[167–171] that borosilicates with the structure of type ZSM zeolites are highly selective catalysts of the synthesis of olefins from methanol. The content of aromatic hydrocarbons in the reaction products obtained[168] at 500 °C and for a 100% degree of conversion of methanol in the presence of borosilicates was 5.4–13.8% and the selectivity with respect to the sum of the C_2–C_4 olefins was 56–70.9%. After treating the borosilicate having the ratio SiO_2/B_2O_3 = 35 with hydrochloric and hydrofluoric acids, its selectivity with respect to olefins increased to 78.9%. The same result was obtained in other investigations[169,170] at a reaction temperature of 550 °C. It is known that the content of olefins in the products obtained in the presence of aluminosilicate zeolites with the same structure (pentasil) and under the same conditions is not more than 20–30%, while the content of aromatic hydrocarbons in C_5 and higher fractions is up to 60–80%.

The appreciably lower catalytic activity of borosilicates compared with aluminosilicates containing approximately the same amount of B_2O_3 has been attributed[135,137,171] to two causes: (1) the catalytic activity of the Si–$(OB)_n$ groups of the silicate skeleton in reactions involving an acid–base mechanism is appreciably lower than that of the Si–$(OAl)_n$ groups; (2) the actual content of boron cations in the silicon–oxygen skeleton at isomorphously substituted sites is extremely low.

3. Elementosilicates with Transition Metal Cations

The catalytic properties of silicates where the Cr^{3+}, Pt^{4+}, V^{4+}, Mo^{6+}, and Zn^{2+} cations were introduced into the initial mixture before hydrothermal synthesis have been investigated[82] in the disproportionation of toluene. The disproportionation was carried out in an atmosphere of hydrogen at a pressure of 400 N cm^{-2}, for the ratio H_2/hydrocarbons = 2, and at temperatures in the range 455–593 °C. The degree of conversion of toluene reached 14–31.8%. The same catalysts were tested in the hydrocracking of the petroleum fraction with T_{nb} = 107–185 °C at a pressure of 70 N cm^{-2}, for the ratio H_2/hydrocarbons = 3, and at temperatures in the range 480–540 °C.[106]

Silicates with the ZSM-5 structure, synthesised in the presence of Cr^{3+}, have been investigated in the alkylation of toluene by methanol. It has been established that the chromosilicates (Cr–ZSM) with SiO_2/Cr_2O_3 ratios of 107 and 38.5 differ in the selectivity of their action from aluminosilicates with the same type of crystal structure (Al–ZSM). For a degree of conversion of methanol of 21–23%, the selectivity with respect to the total xylenes in the presence of chromosilicates was 94–99.2%. The content of *p*-xylene among all the xylene isomers then reached 90.9–58.2%, which is much higher than the equilibrium content (25%). For the chromosilicate impregnated with boric acid, the content of xylenes in the reaction products at 450° and for a degree of conversion of toluene of 20.13% was 86.28% and the content of *p*-xylene among all the xylenes was 74.55% under these conditions. At 500 °C and for a degree of conversion of toluene of 24.1%, these values were respectively 92.36 and 72.7%. The authors[172] suggest that the high *para*-selectivity of the chromosilicates is due to several causes: the influence of diffusion-dependent limitations, a higher concentration of strong acid centres than in aluminosilicates, etc. The ferrosilicates with the crystal structure of zeolites of the pentasil group have been tested as catalysts of the isomerisation of xylenes.[173] The content of *p*-xylene in a mixture of aromatic hydrocarbons containing xylenes and ethylbenzene increased as a result of the isomerisation reactions in the presence of ferrosilicates at 340 °C and atmospheric pressure from 7.4 to 14.5% (to 14.4% in the presence of aluminosilicate), while the content of *m*-xylene diminished from 55 to 40.1%.

The conversion of methanol has been investigated in the presence of a phosphorus-containing silicate with the ZSM structure.[82] The reaction was carried out in an atmosphere of H_2 at a pressure of 3.5 atm, with the ratio H_2/hydrocarbons = 2, and at temperatures of 372° and 400 °C. The specificity of the action of this catalyst compared with aluminosilicate zeolites is difficult to judge on the basis of the data presented,[82] because the content of aluminium in each specimen is not indicated. This precludes the estimation of the influence of the modifying element on the catalytic properties of the silicates synthesised.

Aluminosilicate zeolites with the chabazite and erionite–offretite structures have been synthesised[151] from gels containing sources of boron, titanium, gallium, and zironium. Catalytic data are presented for lanthanum-containing chabazite and erionite. The selectivity in the synthesis of olefins from methanol proved to be higher by 1–2% (82 to 83%) in the presence of these catalysts than in the presence of the H-form of chabazite not containing lanthanum (81%). It was demonstrated in the same studies that the selectivity of the action of type ZSM-5 zeolites, synthesised in the presence of sources of Zr^{4+} and Ti^{4+}, in the synthesis of olefins from methanol is higher by 8–9% (64–65%) than for the usual ZSM-5 zeolite (56%). However data concerning the content of Al_2O_3 in the test specimens and the state of the titanium and zirconium cations are not presented in the above communication.

A detailed study has been made of the catalytic properties of silicates with the structure of ZSM zeolites, synthesised in the presence of transition metal cations but without the addition of sources of aluminium, in reactions involving the synthesis of hydrocarbons from methanol.[129–137] The catalytic properties of the silicates synthesised were compared with those of crystalline silicon oxides having the structure of the ZSM-11 zeolite (silicalite) with the composition $0.02Na_2O.Al_2O_3.1000\ SiO_2$ and obtained by a method analogous to that of Ione et al.[130] At 380 °C methanol is converted to an extent not more than 50% in the presence of silicalite and the main reaction product is dimethyl ether (88–99%); hydrocarbons were also formed in trace amounts. The activity of silicalite was accounted for by the presence of the Al^{3+} admixture at sites isomorphous with respect to those of the Si^{4+} cation. A similar low activity and selectivity with respect to C_2–C_{10} hydrocarbons and a high selectivity with respect to dimethyl ether was shown by silicates containing the V^{4+}, Cr^{3+}, Mn^{2+}, Cu^{2+}, Eu^{3+}, and In^{3+} cations.

According to the data of Vostrikova et al.[134], the degree of conversion of methanol in the presence of manganese-containing silicates was 2–5% and the main reaction product was dimethyl ether. The low catalytic activity was observed both for the specimen where 90% of the manganese (according to EPR data) was in the state of Mn^{2+} ions and for the specimen in which 90% of the manganese introduced was not detected by EPR.

The silicates of the triply charged Ga^{3+} and Fe^{3+} ions as well as beryllium silicates manifested a high catalytic activity in the conversion of methanol into hydrocarbons.[132,133] The selectivity with respect to C_2–C_{10} hydrocarbons at 410–450 °C was 60–98% (Table 11). In the presence of type ZSM-5 and ZSM-11 zeolites, the degree of conversion of methanol under the conditions investigated was not less than 95–98%. The reaction products contained 22–38% of light C_1–C_4 hydrocarbons and 60–70% of liquid hydrocarbons. Mainly propane and butane were detected in the C_1–C_4 fraction, while the C_5 and higher fractions were found to contain aliphatic aromatic alkyl-substituted compounds. The overall content of products agreed on the whole with that quoted in a review.[26] The amount of aromatic hydrocarbons in the reaction product increased with decrease of the ratio SiO_2/Al_2O_3 in the catalyst. Thus, it amounted to 46% for SiO_2/Al_2O_3 = 38 and to only 22% for SiO_2/Al_2O_3 = 280.[137]

A series of studies have been carried out in which the combined substitution of the Si^{4+} cations by aluminium atoms and another cation (Cu–Al, Al–Fe, etc.) was achieved.[174] The introduction of copper or iron ions into the aluminosilicate at the hydrothermal synthesis stage altered the selectivity of their action. Thus, for the same Al_2O_3 content, the amount of aromatic hydrocarbons in the reaction products, obtained from methanol, was less in the presence of aluminoferro- and aluminocupro-silicates and greater in the presence of aluminosilicates. A sharp change in the selectivity of the action of silicates was attained after the complete replacement of Al^{3+} by Fe^{3+} in the latter. Thus the amount of aromatic reaction products did not exceed 10% in the presence of iron silicates whose Al_2O_3 content is at the level of impurities (less than 0.1%) and the Fe_2O_3 content is not less than 1.5%. On the whole, the fraction of aromatic hydrocarbons in the product obtained under the same conditions in the presence of catalysts with identical Al_2O_3 or Fe_2O_3 contents (Fig. 9) diminished in the sequence $SiO_2-Al_2O_3 > SiO_2-Al_2O_3-CuO > SiO_2-Al_2O_3-Fe_2O_3 > SiO_2-Fe_2O_3$.

Table 11. Catalytic properties of silicates with the zeolite structure containing Group I–VIII elements in methanol conversion reactions.

Modifying element	SiO_2/M_nO_m	α, %	Products, wt.%			α, %	Products, wt.%		
			CO, CH_4	DME	C_2–C_{10} hydrocarbons		CO, CH_4	DME	C_2–C_{10} hydrocarbons
		Reaction temperature 380 °C				Reaction temperature 410 °C			
—	1000	2.5	0.4	99.6	—	69.4	2.4	88.1	9.5
Pb	443	41.0	0.2	99.8	—	41.2	3.2	96.8	—
Se	1000	66.0	0.3	99.7	—	76.0	1.7	97.9	0.4
Te	335	6.0	3.0	97.0	—	40.0	0.5	97.5	2.0
Sn	280	25.3	12.3	87.3	—	31.9	21.3	78.7	—
Sb	535	18.0	18.4	81.6	—	29.0	51.2	48.8	—
Eu	1000	25.0	21.5	78.5	—	37.0	46.5	51.2	2.3
Zn	78	5.8	58.3	41.7	—	39.0	80.0	20.0	—
Mn	77	2—5	—	100.0	—	—	—	—	—
Ti	367	2—5	—	100.0	—	29.0	51.2	48.8	—
In	663	29.0	—	100.0	—	57.0	0.4	99.2	0.4
V	480	45.0	—	100.0	—	43.0	—	100.0	—
Cr	112	45.6	7.3	92.4	0.3	61.0	23.0	75.2	1.8
Nd	700	39.0	1.2	97.7	1.1	45.0	1.7	96.6	1.7
Be	91	82.5	0.4	81.0	18.6	87.2	1.1	50.3	48.6
B	46	69.6	1.1	79.0	19.9	74.0	5.3	24.9	69.7
Ga	210	93.5	0.7	6.4	92.9	97.0	0.9	1.0	98.1
Al	58	96.0	0.5	—	99.5	99.6	1.2	—	98.8
Fe	57	84.0	2.0	12.7	85.3	96.5	2.5	2.5	95.0
Fe	109	86.0	0.7	37.4	61.9	92.5	1.2	7.4	91.4

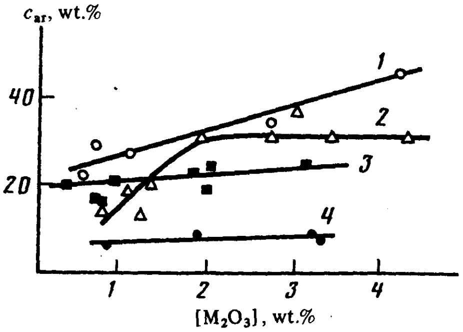


Figure 9. The content of aromatic compounds (c_{ar}) in the hydrocarbon methanol conversion products as a function of the M_2O_3 content in the crystalline silicate with the ZSM-11 structure (for reaction at 380 °C); rate of supply of liquid methanol 1 h^{-1}; composition of silicate: *1*) $SiO_2-Al_2O_3$; *2*) $SiO_2-Al_2O_3-CuO$; *3*) $SiO_2-Al_2O_3-Fe_2O_3$; *4*) $SiO_2-Fe_2O_3$.[174]

Thus, for the same M_2O_3 content in the silicate, the aromatisation reactions proceed at the lowest rate in the presence of iron-containing silicates and at the highest rate in the presence of aluminosilicates. Analysis of the aliphatic component of the hydrocarbons formed demonstrated that the fraction of hydrocarbons with a chain length of C_5 and above diminishes in the same sequence owing to the increase of the fraction of the light C_3–C_4 paraffins and, in the presence of the $SiO_2-Fe_2O_3$ system, also the C_3–C_4 olefins.[174]

A dependence of the rate of conversion of methanol (*k*), referred to one mole of M_2O_3 in a silicate with triply charged cations, on the quantity *e*/*r*, where *e* is the formal charge and *r* the radius of the cation, has been established[137] (Fig. 10). The character of the variation of lg *k* as a function of *e*/*r* does not change when the reaction temperature is raised from 380° to 450 °C: in both cases the curve passes through a maximum. At 380 °C the maximum corresponds to gallium silicate and at 450 °C to aluminium silicate (zeolite). The lowest values of lg *k* were obtained for indium and boron silicates. The maximum content of the C_2–C_{10} hydrocarbons, including olefins and aromatic compounds, in the reaction products was observed for aluminium and gallium silicates; the maximum yield of dimethyl ether was noted in those cases where the amount of hydrocarbons in the reaction products was lowest.

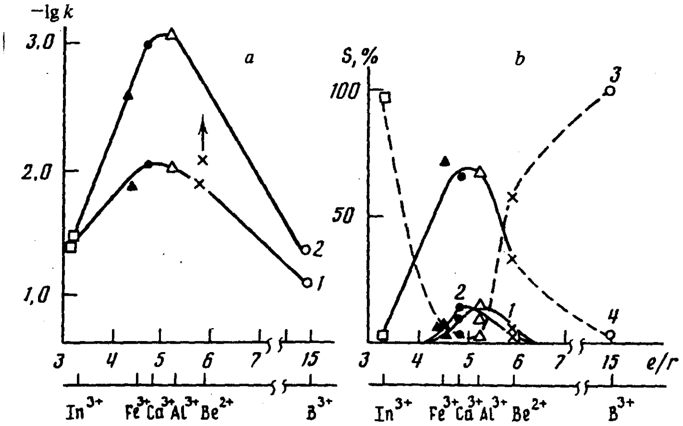


Figure 10. *a*) Dependence of the relative rate of conversion of methanol in the presence of various silicates on *e*/*r* at 380 °C (curve *1*) and 450 °C (curve *2*); *b*) dependence of the selectivity *S* in the formation of various methanol conversion products in the presence of silicates on *e*/*r* at 380 °C: *1*) aromatic hydrocarbons; *2*) isoparaffins; *3*) dimethyl ether; *4*) C_2–C_7 olefins.[137]

VI. CONCLUSION

The results presented in the present review show that silicates with the zeolite structure containing cations of only one type (Si^{4+}) exhibit no catalytic activity in reactions involving an acid–base mechanism. Thus hydrocarbons are not formed from methanol in the presence of silicalite. Silicates with the structure of zeolites, whose multicharged cations are fixed predominantly in an octahedral environment (V^{4+}, Cr^{3+}, Mn^{2+}, Cu^{2+}) and do not therefore enter into the composition of the silicon–oxygen skeleton, do not differ from silicalite as regards the selectivity of their action with respect to aliphatic reaction products. At 450 °C and above, methanol decomposition reactions with the predominant formation of CO and CH_4 (up to 60–90% of all reaction products) take place in the presence of these silicates, which can be due to the catalytic action of the phase comprising the oxides of the corresponding cations.

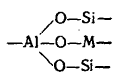
Aromatic hydrocarbons, paraffins, and olefins are formed from methanol in the presence of silicates in which at least some of the cations Fe^{3+}, Ga^{3+}, Al^{3+}, Be^{2+}, or B^{3+} are in a tetrahedral oxygen environment. The EPR and NMR data suggest that the introduction of these cations into the initial gel before the hydrothermal synthesis leads to the formation of active centres having the composition $[Si(OM)_n(SiO)_{4-n}]^{(4-n)-}$.

The dependence of the activity and selectivity of these silicates on the quantity e/r for the cations introduced is not linear, passing through an extremum. The character of the catalytic action is determined by the fact that not only the strength but also the concentration of the active centres depends on the nature of the cation in the silicon–oxygen skeleton. If the length of the M–O bond differs in one direction or another from that of the Si–O bond, then major structural distortions of the silicon–oxygen skeleton should occur. Since the bond length varies in the sequence B–O < Be–O < Si–O < Al–O < Ga–O < Fe–O < In–O, then the greatest distortions in the skeleton are to be expected for the B-, In-, and Fe-containing silicates.

The concentration of the M^{n+} cations in the silicon–oxygen skeleton of silicates should depend on the thermodynamic probability of their fixation in a tetrahedral oxygen environment relative to another, higher, or lower coordination. The energy of the stabilisation of the V^{4+}, Cr^{3+}, Mn^{2+}, and Cu^{2+} ions in an octahedral coordination is very high and the incorporation of these cations in the silicate skeleton in a tetrahedral environment has not been demonstrated. The B^{3+} cations can be fixed in a ternary coordination with a high degree of probability.

The fact that mainly olefins or dimethyl ether are formed from methanol in the presence of silicates containing the B^{3+}, Be^{2+}, and Fe^{3+} cations indicates the slow subsequent conversion of these products into aromatic hydrocarbons and paraffins. Consequently centres having the composition $[Si(OM)_n(SiO)_{4-n}]^{(4-n)-}$, where $M \neq Al$, are much less active in the hydrogen redistribution reactions in unsaturated compounds than the $[Si(OAl)(SiO)_{4-n}]^{(4-n)-}$ groups.

Bonds of the type



may be formed in the synthesis of zeolites (aluminosilicates) in the presence of multicharged cations M^{n+} introduced into the initial silica-alumina gel. For the same Al_2O_3 content, silicates without additives have a higher concentration of the $[Si(OAl)_n(SiO)_{4-n}]^{(4-n)-}$ centres with high values of n than the silicates incorporating the M^{n+} cations.

The introduction of multicharged cations, capable of substituting the Si^{4+} and Al^{3+} cations isomorphously, into aluminosilicates (zeolites) should therefore diminish the number of aluminium atoms in a single active centre and hence the ability of the latter to accelerate the hydrogen redistribution reactions in unsaturated compounds.

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Study of Converse Problems in Chemical Kinetics as a Method for the Investigation of the Mechanisms of Complex Reactions

E.F.Brin

The application of mathematical modelling methods to the determination of the mechanisms of complex chemical reactions is considered. On the basis of the analysis of the present state of the mathematical modelling of chemical kinetic processes, it is shown that the study of converse problems constitutes an extension of the traditional kinetic approach to the construction of models. A classification of the direct and converse problems in chemical kinetics is proposed. It is shown that converse problems are of greatest interest at the present time in the identification of the chemical type of the reaction mechanism. The bibliography includes 133 references.

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I. INTRODUCTION

The determination of the mechanisms of chemical processes is a complex physicochemical problem, whose solution is based on the fundamental postulates of theoretical chemical kinetics and on experimental studies.[1-3] The development of computer techniques and progress in the mathematical methods used in chemistry have altered qualitatively the role of mathematical modelling in the solution of this problem, having converted it into a method for the investigation of the mechanisms of chemical reactions just as legitimate as other procedures.[4-6] However, in most studies on the application of mathematical modelling in chemical kinetics,[7-15] mainly probability-statistical and computational aspects of the problem of the construction of models are considered and due attention is not paid to the kinetic aspect. The present review is devoted to the analysis of the present state of precisely this, kinetic aspect.

II. STUDY OF CONVERSE PROBLEMS IN CHEMICAL KINETICS AS A DEVELOPMENT OF THE KINETIC APPROACH TO THE CONSTRUCTION OF MODELS

One of the main ways of investigating the mechanisms of chemical reactions involves the kinetic approach.[16,17] The term reaction mechanism has usually come to be understood as the set of chemical stages making up the process.[5,18] In a broader sense, the word mechanism includes fundamental kinetic characteristics of the process such as the determination of the active species in the reaction, the ratios of the rates of the individual stages, etc.[4,13,19-22] (to make the treatment concrete, this type of mechanism has been called[22] the kinetic type of reaction mechanism).

The modelling method in the kinetic approach is based, on the one hand, on the kinetics of reactions of different classes and, on the other, on experimental design, which makes it possible to isolate and investigate quantitatively certain small fragments of the overall kinetic scheme.[4,17] A logical application of this approach permits the determination of the mechanism of the entire process, including the kinetic parameters of the stages. Indeed the majority of the mechanisms known at the present time have been deduced in precisely this way.[8-10,17,23] The success of this method has been to a large extent associated with the development of ideas about radical chain reactions.[1,24,25]

The modelling procedure in the kinetic approach includes three main stages:[4,5,17,22,26] (1) the purposeful collection of information, including the establishment of a tentative kinetic scheme process; (2) the selection of experimental methods on the basis of data obtained in the first stage and the design and carrying out of the experiment; (3) the kinetic-mathematical analysis. The application of the methods of computational mathematics and of the qualitative theory of differential equations in all the three stages of the modelling process[9] made it possible to isolate as the object of study a kinetic model of the process (i.e. a system of differential chemical kinetic equations).[17,27] The problems involved in the construction of such models reduce to problems involving the recovery of the right-hand sides in the systems of differential equations, which have come to be called the converse problems in mathematical physics.[28-30] Thus the converse problems in chemical kinetics are, in a broad sense of the term, problems involved in the determination of the reaction mechanism.[9,17,31] In essence, the converse problems involve the extension of the kinetic approach to processes whose models cannot be investigated without using computer techniques.

The specific content of each stage in the study of the mechanism is determined in the first place by the aim of the mathematical model.[5] Accordingly, it is possible to distinguish two large classes of converse problems;[32] the first class includes the converse problems whose study is used as a method for the investigation of the mechanisms of complex chemical reactions and the second includes converse problems in which mathematical models are a means for the solution of practically important problems of control, optimisation, prediction, etc. (target converse problems).

The traditional formulation of the converse problems in chemical kinetics[4,17,18,32,33] assigns primary importance to the rate constants for elementary reactions. It is assumed that, provided that the values of all the constants are known, the mathematical model of the process is defined and can be used for the solution of the target problems. For reactions of simple types, such formulation of the problem[18,35] is correct and the problems involved in setting up mathematical models, in the determination of their adequacy, and in the estimation of the parameters are in essence solved simultaneously.

However, one should not apply mechanically such formulation of the converse problem in the consideration of reactions of complex types (chain, autocatalytic, and such processes) also because, in relation to complex processes, the converse problems are solved as a rule under conditions of an acute deficiency of experimental data, as a result of which the solutions obtained are ambiguous.[4,17–22,33–36] This ambiguity has in fact led at one time to a natural lack of confidence by experimenters in the results obtained from the solution of converse problems.[33,35] Evidently the ambiguity of the solution obtained can be eliminated by improving only the experimental technique and not the numerical method.[30] Thus some modification of the formulation of the converse problems is essential.[30]

In the first place, we may note that the formulation of the converse problem for reactions of complex types should vary depending on the aim in constructing the model and on the amount of *a priori* information about the process mechanism. Thus, for processes whose kinetics are known beforehand (i.e. with a known kinetic type of reaction mechanism[22]), the aim of the investigation is the determination of the unknown rate constants. In this case special kinetic experiments are used to solve the problem.[4,18,23,33,37–40] As a rule, the use of such problems is correct when the amount of experimental data is sufficient. The necessity to develop special experimental techniques for virtually each specific problem, their uniqueness, and high cost led to their comparatively rare employment when the aim of the study is to obtain a mathematical model of the process reflecting adequately the main kinetic features. In this case experimental methods are used to solve the problems whereby one can record the kinetics of the changes in the concentrations of comparatively stable reaction components[4,18] or to measure the steady-state reaction rates.[4,8,10–14] In this situation the mathematical model of the process is not determined by the rate constants themselves but by certain combinations of the latter,[9,10,17–23,41–46] whose determination can sometimes be the aim of the solution of the converse problem—the identification of parameters.[42]

The main deficiency of the kinetic approach when such experimental information is available consists in the fact that the measurements refer to the rates of slow stages and do not yield information about the rates and presence of faster stages,[48] i.e. about the kinetics of conversion of the active components of the reaction. Evidently, in the absence of *a priori* information about these kinetic features, the formulation of the problem of the parametric identification becomes pointless and the problem of the identification of the mechanism (more precisely the kinetic type of mechanism) of the reaction comes to the fore. Indeed, the kinetic scheme of the process contains no information about the reactivity of the reaction components and about the relative contributions of the stages to the overall process. In the absence of such information, it is impossible to isolate beforehand the combinations of constants determining the course of the process. Accordingly, there is also a change in the specific aim of the study, which consists in this instance in the determination of the kinetics, i.e. of the possible reaction mechanism.[13,21,26]

The most obvious way of obtaining information necessary for the determination of the possible mechanism consists in a direct experimental measurement of the varying concentrations of the intermediate reactive reaction components. However, as already stated, the high cost and complexity of the methods limits significantly the applicability of this approach.[4,17,23,37,49] The availability of experimental methods whereby the kinetics of the conversion of the "slow" reaction components or the steady-rates of the stages can be recorded has made such an experiment the main procedure for the determination of the possible reaction mechanism. The dependence of the initial or steady-state rates, induction periods, and other macrokinetic parameters under experimental conditions, for example, on the initial concentrations, does indeed frequently permit the determination of the reaction mechanism[8–15,23] on the basis of which it is possible to set up an adequate mathematical model.

The converse problems in chemical kinetics, which result from the natural extension of the kinetic approach, possess not only all the advantages but also all the disadvantages of the latter. Within this framework, it is impossible to demonstrate that the true reaction mechanism has been established[48] and one can only speak of the lack of contradiction between the mathematical model, corresponding to the mechanism obtained, and the existing experimental data,[4,19] i.e. of the possibility that such a mechanism can occur. The term "identification" should also be understood in precisely this sense.

The mathematical and computational aspects of the problem have been described fairly completely in the literature and here we shall specify only certain problems of a mathematical character, whose solution determines the real possibility of formulating the converse problems of chemical kinetics: (1) experimental design;[13,30,42,49,50] (2) the choice of the functional determining the similarity between the experimental and calculated values of the observed variables;[26,42,50–54] (3) the selection of a method for the integration of the system of potential chemical kinetic equations;[4,13,17,20,26,55–63] (4) the selection of a method for the minimisation of the functional.[4,11,13,19–21,42,50,52–55,63–74]

III. DIRECT PROBLEMS IN CHEMICAL KINETICS

In chemical kinetics the course of the process is determined by the time variation of the concentrations of the reactants. This dependence constitutes the information obtained from the study of the chemical process. The derivation of this information by the mathematical modelling of the chemical process is understood as the direct problem.[18] To make the treatment concrete, we shall consider processes for which the variation of the concentrations of the reactants (x) is specified unambiguously by the Cauchy problem:

$$\frac{dx}{dt}=f(x);\ x(0)=x^0. \tag{1}$$

This system[6,17,27] constitutes a kinetic model of the chemical process. The form of the right-hand side of Eqns.(1) is determined by a set of kinetic postulates,[17,75] which can be formulated in the following manner for the processes involved in isothermal equilibrium chemical kinetics in closed systems and which are mainly considered in this review.

1. The chemical process can be represented by a set of elementary stages:

$$\sum_{i=1}^{N}\nu_{ij}^{+}A_i\to\sum_{i=1}^{N}\nu_{ij}^{-}A_i;\quad j=1,2,\ldots,M, \tag{2}$$

where A_1, A_2, ..., A_N are the components participating in the reaction and ν is the stoichiometric matrix ($\nu_{ij}=\nu_{ij}^{+}-\nu_{ij}^{-}$; the plus and minus signs correspond to the stoichiometric coefficients of the reactant entering into the jth reaction and formed in it).

2. The relation between the rate of the elementary stage w_j and the concentrations of the reactants involved in it, $x_i = [A_i]$, is determined by the Law of Mass Action:

$$w_j = k_j \prod_{i=1}^{N} x_i^{\overset{+}{\nu}_{ij}} , \qquad (3)$$

where k_j is the rate constant for the jth stage.

3. The overall rate of conversion of the ith reactant is determined by the principle of the independence of the occurrence of the elementary stages:

$$\frac{dx_i}{dt} = \sum_{j=1}^{M} \nu_{ij} w_j \qquad (4)$$

Thus, for the situation considered, the kinetic model of the process is specified by (1) the stoichiometric matrix ν and (2) by the initial concentrations and the rate constants.

The kinetic model should reflect the asymptotic character of the chemical process (the rapid attainment of steady-stage regimes with respect to the concentrations of the active reactants and the negligible contribution by the rates of certain stages to the rates of change in the concentrations of the reactants). We shall put Eqn.(1) in the following form:

$$\tau_i \frac{dx_i}{dt} = \varphi_i(x, k); \; i = 1, 2, \ldots, N; \qquad (5)$$
$$x(0) = x^0 ,$$

where

$$\varphi_i(x, k) = \sum_{j=1}^{M} H_{ij} \nu_{ij} w_j . \qquad (6)$$

Here $k = (k_1, k_2, \ldots, k_M)$ is the rate constant vector and τ_i and H_{ij} are parameters. We may note that Eqn.(1) is a special case of Eqn.(5) when $\tau_i = 1$ for all i and the elements of the matrix H_{ij} are determined for non-zero ν_{ij} and are unity.

We shall define the kinetic model as a special model in relation to Eqn.(1), provided that there exist parameters τ and H in Eqn.(5) such that, when $\tau_s \to 0$ ($s = p + 1, \ldots, N$) and $H_{mn} \to 0$, the system of Eqn.(1) is converted into a system

$$\frac{dx_i}{dt} = \varphi_i(x, k); \quad i = 1, 2, \ldots, p , \qquad (7)$$
$$0 = \varphi_i(x, k); \quad i = p + 1, \ldots, N$$

such that, over a certain time interval $t \in (t_1, t_2)$ and in a certain range of initial concentrations $x^0 \in X$, the following inequality holds:

$$|x(t) - \tilde{x}(z)| < \varepsilon , \qquad (8)$$

where $\tilde{x}(t)$ is the solution of Eqns.(7) and ε is a certain specified accuracy [for example the accuracy of the numerical integration of Eqn.(1)]. For convenience, we assume that the method of steady-state concentrations is applicable to the last $N-p$ reactants. The parameters H_{mn} will be set equal to zero, provided that the rate of the nth stage in the mth equation can be neglected.

We set up[32,42] a correspondence between the observations vector $\eta(t)$, in which account is taken of both the incompleteness and errors of the measurement, and the vector $x(t)$, which is a solution of Eqns.(1) or (7):

$$E(\eta(t)) = Rx(t) , \qquad (9)$$

where E is the symbol of the mathematical expectation of a random quantity and R a square matrix. In the general case, for example, in spectrometric measurements, the matrix R can be non-diagonal and can include spectral parameters. However, the matrix R is fairly often diagonal, i.e. measurements are made of the concentrations themselves and the diagonal elements of R are identical with the parameters of the vector τ or rank$(R) < N - p$. This situation will in fact be mainly analysed in the present review.

The procedure where the vector $\eta(t)$ is brought into correspondence with the vector-function $f(x, k)$ set up on the basis of Eqns.(1) will be referred to as the general direct problem and will be regarded as complete if rank$(R) = N$; otherwise it will be regarded as truncated.[32] The procedure in which the vector $\eta(t)$ is brought into correspondence with the vector-function $\phi(x, k)$ set up on the basis of Eqns.(7) will be referred to as the special direct problem.

Thus each direct problem is determined by the rules governing the construction of the right-hand sides of the equations, the stoichiometric matrix, the kinetic parameters and the law (R) relating the exact solution $x(t)$ to the observations vector $\eta(t)$.[32] For special direct problems, an essential intermediate link between the rules governing the construction of the right-hand sides, including the specification of the stoichiometric matrix, and the rules determining the kinetic parameters and the law (R) is the rule according to which the transition to the system of differential-algebraic Eqns.(7) is effected.

Evidently, depending on the values of the rate constants, the selected time interval, and the initial concentration range, different special problems correspond to the solution of the general problem [in the sense of the fulfillment of inequality (8)]. For this reason, before formulating the converse problem, we shall consider the classification of special kinetic models.

IV. SPECIAL KINETIC MODELS

We shall divide the kinetic models into two large classes. For models of class 1 (referred to by convention as the "chain" class), there are no linearly dependent equations among the algebraic components of Eqns.(7). For models of class 2 (the "catalytic" class), certain algebraic equations in the system (7) are linearly dependent. From the standpoint of kinetics, this means that a stationary regime with respect to the concentrations of the initial reactants is not established in "chain" processes, while in "catalytic" processes there is a possibility of the attainment of a stationary regime with respect to the concentration of the catalyst, which is a starting material. For "catalytic" processes, we eliminate from Eqns.(7) the linearly dependent equations and supplement the system by the material balance equations. Bearing in mind that certain concentrations involved in the material balance can be negligible, we introduce the parameters $\tilde{h}$ into the material balance equation. For example, in the case where the system contains one equation which is a linear combination of the remaining equations, we have

$$\sum_{i=p+1}^{N} \tilde{h}_i x_i = c^0 , \qquad (10)$$

where $\tilde{h}_i = 0$ provided that the concentration of the ith reactant in Eqn.(10) can be neglected, whilst otherwise $\tilde{h} = 1$ and c^0 is the initial concentration of the catalyst.

Evidently the selection of the elements of the vector τ and of the matrix H is not arbitrary in the general case. Thus τ_i can be zero only for intermediate reactants or the catalyst. Under these conditions, the choice of $\tau_i = 0$ determines to a large extent the choice of the elements of the matrix H. Indeed, in order that stationary conditions should hold with respect to all the intermediate reactions, it is essential that the following system be soluble:[18]

$$\sum_{j=1}^{M} \nu_{lj}\mu_j = 0 \quad , \tag{11}$$

where l are the numbers of the intermediate reactants (suppose that $l = p_1 + 1, \ldots, N$, where $p_1 < p$) and μ_j are the stoichiometric numbers of the stages.

The sum of the stages, taken with the corresponding stoichiometric numbers which are selected so that the overall stoichiometric reaction equation does not include intermediate species (for a stationary regime, the active intermediate species), is referred to as the reaction pathway[76-79] and determines a certain general kinetic model with lower dimensions:

$$\frac{dy}{dt} = \psi(y, \varkappa); \quad y(0) = y^0; \quad y = (y_1, y_2, \ldots, y_{p_1}) , \tag{12}$$

where $y_i = x_i$ for $i = 1, 2, \ldots, p_1$.

Evidently the choice of the stochiometric numbers must ensure that Eqn.(11) holds for $l = p + 1, \ldots, N$ and does not hold for $l = p_1 + 1, \ldots, p$. Here the elements of the matrix H must be unity, provided that the corresponding $\mu_j \neq 0$ and must be zero in the opposite case. The elements of H not entering into the algebraic component of Eqns.(7) are selected arbitrarily.

We shall illustrate this procedure in relation to a catalytic reaction:[18]

	Stages	Pathways		
		I	II	III
(1)	$E + S \rightarrow ES$	1	1	2
(−1)	$ES \rightarrow E + S$	1	0	1
(2)	$ES \rightarrow E + P$	0	1	1

Here S is the substrate, E the catalyst, and P the reaction product. On the assumption of the stationary character of the reaction, the equation determining the stationary condition is

$$\mu_1 - \mu_{-1} - \mu_2 = 0 \tag{13}$$

By choosing the smallest positive integral solutions of this equation, we find that three pathways (I–III) can be realised in the given system and that each pair of pathways is linearly independent.

We shall consider the balance equation

$$\tilde{h}_1[E] + \tilde{h}_2[ES] = [E]^0 . \tag{14}$$

Evidently, three ways of selecting the parameters $\tilde{h}_i$ in Eqn.(14) are possible: (1) $\tilde{h}_1 = \tilde{h}_2 = 1$; (2) $\tilde{h}_1 = 1$, $\tilde{h}_2 = 0$; (3) $\tilde{h}_1 = 0$, $\tilde{h}_2 = 1$. Thus, in the given system nine special models will formally correspond to the single general kinetic model. For example, for the second pathway, the following special model exists:

$$\frac{dx_1}{dt} = -k_1x_1x_3 \ ,$$
$$\frac{dx_2}{dt} = k_2x_4 \ ,$$
$$k_1x_1x_3 - k_2x_4 = 0 \ ,$$
$$x_4 = x_3^0 \ ,$$

where $x_1 = [S]$, $x_2 = [P]$, $x_3 = [E]$, and $x_4 = [ES]$. The general kinetic model with lower dimensions corresponding to this special model then has the following form:

$$\frac{dx_1}{dt} = -k_2x_3^0 \ ,$$
$$\frac{dx_2}{dt} = k_2x_3^0 \ .$$

We may note that the determination of the general kinetic model with lower dimensions is possible only if the algebraic component of Eqns.(7) is soluble in an explicit form in terms of the concentrations of the reactants with respect to which a stationary regime is established.[19] However, the asymptotic character of the behaviour of kinetic systems increases significantly the probability of obtaining an explicit form of such models. For example, this has been achieved for extremely complex processes involving the joint oxidation of hydrocarbons.[80,81]

A definite asymptotic form of Eqns.(1) or a definite kinetic feature of the reaction corresponds to each set of numbers τ_i, H_{ij}, and $\tilde{h}_i$. A definite reaction regime has been brought into correspondence[80] with each asymptotic type of this kind. When the range in which the initial concentrations are specified or the degree of conversion is altered, the regime can change. The set of regimes which can be realised in the system for the specified rate constants determines the kinetic type of the reaction mechanism.[22] Evidently a certain region in the rate constant space, in which specific asymptotic properties of Eqns.(1) are manifested, corresponds to each kinetic type of reaction mechanism. This region has been defined[22] only for "chain" processes (in the form of the ratio of the rates of elementary stages).

The solution of the direct problems in chemical kinetics is comparatively rarely the aim in itself; these problems [like the mathematical problem of integrating Eqns.(1) or (7)] are usually a component of the converse problems. One can indicate only one important feature associated intrinsically with their solution: the elucidation of the question of which special kinetic models correspond to the general model [in the sense of the fulfillment of inequality (8)] when the rate constants are known or within a certain range of rate constants and for specified ranges of the initial concentrations and a specified time interval.[4,17,26,63,82,83]

In other words, this problem consists in determining the kinetic type of the reaction mechanism. For example, in the solution of the problem for the methane oxidation reaction, it has been shown[26,63] that, up to 1600–1700 K, the course of the process is determined by the chain reaction regime, while at higher temperatures it is determined by the free radical reaction regimes; for the ethane oxidation reaction,[84] the kinetic type of the reaction mechanism is determined by the regime in which degenerate branching is associated with the decomposition of performic acid or of the superperoxy-radical and not with the reaction $CH_2O^{\bullet} + O_2 \rightarrow HCO^{\bullet} + HO_2^{\bullet}$, as had been assumed earlier. Gontkovskaya et al.[85] considered five reaction regimes and Dimitrov[17] considered six reaction regimes in the combustion of hydrogen as a function of conditions. The reaction regimes in the liquid-phase oxidation of hydrocarbons have been investigated.[4,81,86] The direct problem has been solved[87,88] in order to test the correspondence between the approximate formula for the calculation of the inhibition period in the inhibited oxidation hydrocarbons, obtained on the basis of a special kinetic model, and the exact values of this quantity obtained by solving the general direct problem.

V. CLASSIFICATION OF THE CONVERSE PROBLEMS IN CHEMICAL KINETICS

If the direct problems are considered as problems of discovering one realisation $\eta(t)$ of a certain structure, determined by the rules governing the construction of Eqns.(1), (9) or (7), (9), then the converse problems can be naturally interpreted as the recovery of the elements of this structure from the set of observations $\eta(t)$.[32] The rules governing the construction of the realisation $\eta(t)$ are regarded as statistical hypotheses.

We shall consider these hypotheses for isothermal chemical kinetic processes in which it is assumed that the following parameters are known: Π_1—the matrix for ν_{ij}; Π_2—the law relating the rate of the elementary stage to the concentrations, for example, Eqns.(3); Π_3—the expression for the total rate of conversion of all the reactants, for example Eqn.(4); Π_4—the limiting transition to which corresponds the the solution of the partial direct problem, or the absence of such a transition; Π_5—the kinetic parameters.

The system of hypotheses Π_1–Π_5 determines the general kinetic model and its corresponding special models. We shall supplement this system by hypotheses C, defining the model of observations, in which the following parameters are assumed to be known: C_1—the matrix R; C_2—the form of the distribution of experimental errors (with an accuracy to within the values of the parameters); C_3—the parameters of the distribution.

This system makes it possible to construct a hypothetical solution to the direct problem and to compare it with the existing set of experimental data $\eta(t)$. It is natural to consider the converse problems in chemical kinetics as problems of the recovery of the unknown hypotheses in this system from the known set of $\eta(t)$. The converse problems associated with the recovery of the hypotheses C_2–C_3 are outside the framework of this review. Their recovery requires as a rule the formulation of special statistical experiments.

The form of the matrix R is in most cases not known exactly. When different spectrometric measurements are performed, the matrix R frequently includes unknown parameters (for example, the absorption coefficients in spectrophotometric measurements[72]), which also have to be recovered in the solution of the converse problems. However, for simplicity, we shall assume that the matrix R is fully defined.

It is easy to note that, in the formulation of the direct problem, a hierarchy of hypotheses Π_l arises and consists in the fact that a definite content cannot be attributed to the hypothesis Π_s if the hypothesis Π_{s-1} has not been formulated. The pointlessness of formulating the converse problem as the problem of recovering the hypothesis Π_s when the hypothesis Π_{s-1} is unknown follows from the hierarchy of hypotheses. It is evident that, for example, the formulation of the problem of finding the rate constants has no significance if it is not known *a priori* whether the Law of Mass Action holds.

As a rule, having at ones disposal a set of observations, it is possible to state beforehand whether we are dealing with a complete [rank(R) = N] or truncated [rank(R) < N] solution of the direct problem. The situation is different as regards the question whether the above set of observations is a result of the solution of the general or special direct problems. In fact, in a real situation we are always dealing with a solution of the general problem and the limiting transition to the special problem is merely a mathematical reflection of the characteristic features of the chemical reaction.

We shall refer to the converse problem as general if it is known that there is no limiting transition in which it is impossible to distinguish the solutions of the general and special direct problems for a specified experimental accuracy. Otherwise we shall refer to it as a special converse problem.

The asymptotic character of the behaviour of chemical processes and the difficulty of the experimental measurement of the changes in the concentrations of all the reactants are due to the same physicochemical causes. The times during which the process begins to be determined by the special kinetic model amounts to millionths of a second (and less). This creates experimental difficulties in the study of the kinetics before the attainment of a stationary regime. Furthermore, in view of the high reactivity of the "fast" reactants, their concentrations are low (down to 10^{-12} M) and their experimental determination also gives rise to difficulties at the present time. Thus the deficiency of experimental data at the disposal of investigators in the solution of converse problems with deep physicochemical roots and the success of the solution are in many respects determined by the availability of *a priori* data on the process investigated.[22]

The extent to which the chemical process has been studied, i.e. the availability of information about Π_1–Π_5, determines the level of the converse problem.[32] The zero level corresponds to the case where all the factors constituting the direct problem, including the parameters, are known. The converse problem at this level consists in testing the consistency of the general or special kinetic model with the available set of experimental data. The converse problems at this level have been solved, for example, by Emanuel' and co-workers.[89–91] Evidently, whatever the level of the converse problem, the question of consistency is the first to which it is essential to obtain an answer in the course of its solution.

The usual formulation of converse problems as problems involving the determination of unknown kinetic parameters[5,14,17–22,26,35,41–45] on the assumption that information about Π_1–Π_4 is known beforehand belongs to the first level. A systematic approach[92] has been made[42] to the consideration of mathematical models of chemical kinetics. The term model is understood as a rule governing the transformation of the input variables into output variables, established by the analysis of causal-consequential relations:[93]

$$\eta(x(t)) = B\{t, \varepsilon, \theta\}\,, \qquad (15)$$

where $B\{.\}$ is an operator transforming the variables t, ε, and θ (where t is the time, ε are random factors, and θ are unknown parameters) into the observed variables η. Following the terminology proposed by Gorskii,[42] we shall define the converse first level problem as the problem of parametric identification arising in the case where the structure of the model, expressed by the operator $B\{.\}$, is known *a priori*. Otherwise, problems of structural identification arise—the converse problem at higher levels. The second level problems are associated with the recovery of hypothesis Π_4 for specified Π_1–Π_3, i.e. with the establishment of the kinetic type of the reaction mechanism.

The third and fourth level problems are associated with the recovery of the principal postulates of the chemical kinetics. In fairly numerous instances, for example, when reactions occurring under the conditions of a high density of the external energy flux (shock tubes, molecular beams, plasmachemical processes, etc. are considered), one cannot use the usual Arrhenius kinetics.[26,40,63] For a correct formulation of the kinetic postulates, it is essential to find the distribution of the excited species with respect to states. Thus the given problems refer to the generalised non-equilibrium chemical kinetics[94] and extend far outside the framework of the present review. Analysis of studies concerning non-equilibrium chemical kinetics has shown that, as a rule, the mathematical models for such processes are obtained within the framework of a physicochemical and not a kinetic approach.[17]

The fifth level problems are associated with the selection of one of several versions of the kinetic schemes for the process. If each such version (hypothesis) does not necessitate the reformulation of the fundamental postulates of chemical kinetics, a definite special kinetic model corresponds to it.

Thus in the case of equilibrium Arrhenius chemical kinetics, the second and fifth level problems actually refer to the same level.

1. Converse First Level Problems

When problems are considered at this level, account must be taken of the degree of completion and generality of the formulation of the direct problem with the aid of the solution of which a set of η_{ij} is believed to be obtainable. If a complete solution of the general direct problem is available, i.e. the kinetics of the variation of the concentrations of all the reactants in the time interval $t \in [0, T]$ have been determined experimentally, the problem has been correctly formulated.[34,36,45] The question of the validity of the formulation of the converse problem for the case where a truncated solution of the general direct problem is available (measurements are not made for all the reactants) or for the complete solution of the special problem (measurements are made for all the reactants in the stationary regime) can be elucidated for each specific problem. In the general case (truncated solution of the special problem), the formulation of the problem is as a rule incorrect.[4,17,18,20–22,33–36,41–45,95] From the physicochemical standpoint, such formulation is equivalent to an attempt to extract more information from experimental data than the latter contain.[4,19] Indeed the solution of the special truncated direct problem agrees in this case [in the sense that Eqn.(8) holds] with the solution obtained by the integration of the general kinetic model with lower dimensions [Eqn.(12)].

Thus the attempt to find all the rate constants reduces to the recovery of the concentration dependences for the "rapid" reactants which do not enter into Eqn.(12) at all.[41] From the mathematical standpoint, the causes precluding the solution of the problem in terms of the traditional formulation are as follows:[54] (1) the inadequate information extractable from the measurements; (2) a significant non-linearity of the kinetic models in terms of the constants being solved; (3) different sequences in the initial set of experimental data; (4) the lack of information about the fundamental statistical characteristics of the measurement. These causes are a consequence of the physicochemical characteristic of the processes (the asymptotic character of their behaviour), which were considered above.

Thus the solution of the problem of finding the rate constants gives rise to difficulties not as a result of any mathematical causes but by virtue of the complexity and the considerable labour involved in the extraction of sufficient experimental information.[19,20]

Regardless of the purpose for which the model has been constructed, the converse problem at the first level consists of two components:[20,21] the first significant component includes the test of the consistency of the proposed kinetic model with the available set η_{ij} of experimental data; the second, target component involves the extraction from the experiment of information about the process mechanism which is essential for the construction of the model. The fact that in the observation range the process is described by a special kinetic model and an umambiguous determination of the rate constants is therefore impossible clearly indicates a way of modifying the formulation of the converse problem. The first component of the problem then consists in finding a function from the class defined by Eqns.(1) which agrees [in the sense of Eqn.(8)] with the function from the specified class (7) providing the best description of the experimental data. The possibility of passing to a general model with low dimensions [Eqn.(12)] makes it possible in many instances to formulate the problem as one involving the finding of a function from the class defined by Eqn.(12). However, having solved this problem, it is essential to test whether rate constants having a physical significance, for which Eqn.(8) holds, do exist. Thus the first part of the converse first level problem can be formulated as follows: do parameters k or κ such that the kinetic model is not rejected for the given level of significance, actually exist? Hence follows the most frequently encountered formulation:[14,17,26] the aim is to find the parameters k or κ ensuring a maximum in the probability function.

Having solved the first part of the problem, it is possible, on the basis of the purpose for which the model has been constructed, to formulate the second part, which may consist in finding the unknown rate constant k or the unknown combinations of constants κ or the aim may be to reach a conclusion about the behaviour of the process.

2. Problems of Parametric Identification

The problem of finding unknown rate constants arises as a rule when a large amount of *a priori* information is available about the process, i.e. when many rate constants and some of their ratios are known. Special experimental kinetic studies are then performed,[37–39] which make it possible to estimate or revise a comparatively small number of constants. The vast majority of the values of the rate constants for elementary reaction known at present[35,96] have been obtained as a result of this approach.

For example, the aim of the study of the interaction of fluorine with halogens near the self-inflammation limit was the revision of the rate constants for the branching and energy chain termination reactions.[72] The experiments were performed under the conditions in the development of the branching-chain process, whose mechanism and the majority of rate constants were known.[97] The problem proved to be correctly formulated and the required parameters were estimated on a computer. An analogous investigation of the hydrogen combustion reaction[52] made it possible to revise four of the ten rate constants on the basis of the dependence of the maximum concentration of the radicals on the initial conditions. The solution of these converse problems does not give rise to fundamental difficulties. The methods developed[10,20,26,52,53,61,83,98] (see also the studies quoted by Gorskii[42]) have been applied successfully with this aim also in the study of reactions of simple types.[18,99,100]

The practically important properties of the process are often determined by the kinetics of the variation of the concentrations of the "slow" reactants. In this case the system of Eqns.(12) constitutes a model of the process and both parts of the converse first level problem can be combined in a single problem of the identification of the parameters κ. In many instances the parameters κ themselves determine the practically important properties of the process investigated and their determination is the aim of the solution of the converse problem, for example in tests.[101,102] This formulation of the converse problem also generally proves to be correct. Combinations of the rate constants have been estimated, for example, for the pyrolytic reactions of ethane,[20,61] the joint oxidation of hydrocarbons,[10,81,103] and the liquid-phase oxidation of tetralin [104] and in the study of the decomposition of hydroperoxides,[105] the initiated oxidation of hydrocarbons in the presence of inhibitors,[101,102] etc.

The formulation of the converse problem is used especially frequently in the study of heterogeneous-catalytic reactions. Thus the parameters κ have been estimated for the n-butene dehydrogenation reactions,[106] the interaction of ethane with water vapour,[107] the hydrogenation of oxo-synthesis aldehydes,[108] the isomerisation of higher olefinic hydrocarbons,[109] the dehydrogenation of n-butane,[110] the hydrogenation of phenol[13] and benzene,[11] the oxidation of carbon monoxide,[111] etc. A more detailed bibliography on the solution of the converse problems in the study of heterogeneous-catalytic processes can be found in a number of other communications.[5–15,26,27,50]

The combinations of rate constants obtained can be used to revise the intrinsic rate constants using the results of the corresponding experiment or using *a priori* information about certain rate constants.[103]

3. Target Converse Problems

The situation where both parts of the converse problem are solved simultaneously[21,62] was considered in the previous subsection. The validity of the formulation of this problem ensures the uniqueness of the solution of the parametric identification problem. The availability of such solutions makes it possible to test the hypothesis about the adequacy of the process model. In the general case the transition to a general kinetic model with lower dimensions is not always justified: any set of constants satisfying the physical significance (or the specified form) of the special kinetic model and ensuring an adequate description defines a mathematical model which can be used to solve target problems.

As examples of the solution of the first part of the converse problem, we may point to studies on the modelling of the oxidation of tetralin,[104] the radiation-initiated isotope exchange of deuterium with the hydroxy-groups of silica gel,[26] the oxidation of methylacrolein,[112] the oxidation of ethylbenzene in the presence of aromatic amines and bivalent copper compounds,[113] the coupled oxidation of hydrocarbons,[114] the oxidation of coconut oil,[115] the sulphonation of secondary alcohols,[116] the catalytic oxidative dehydrogenation of n-butene,[117] the oxidative regeneration of aluminosilicate cracking catalysts,[118] the cyclooligomerisation of butadiene,[119] the oxidation of methanol,[120] the photochemical oxidation of polyolefins,[121] the oxidation of anthrahydroquinone,[122] the liquid-phase oxidation of *p*- and *m*-di-isopropylbenzenes,[123] the oxidation of carbon monoxide,[124] the hydrochlorination of acetylene,[125] etc. In these studies the rate constants were used solely as a means for the parametric test of the hypothesis of the adequacy of the corresponding mathematical models.

When the problem of adequacy has been solved positively and solution (1) has been found, one can proceed to the solution of a particular problem for which the mathematical model has been constructed. Formulation of such target problems will be considered in relation to kinetic prediction problems.[3,126] Suppose that one needs to test the truth of the claim that the target function $\phi[x(k)]$ belongs to the region u. For this problem, there may be three solutions: (1) "yes", i.e. $\phi \in u$ and the probability of the error is less than β, (2) "no", i.e. $\phi \notin u$ and the probability of error is less than α, and (3) the amount of experimental data for a well-founded answer for the specified α and β is small. Here α and β are respectively errors of the first and second kind.

4. Allowance for the *a priori* Information in the Solution of Converse First Level Problems

Evidently first level problems arise when sufficient *a priori* information is available about the process mechanism: the mechanism must satisfy a whole series of various requirements, which make it possible to formulate the hypotheses Π_1–Π_4. The need to take into account the *a priori* information in the formulation of converse problems has already been pointed out.[14,17,20,22,26] The range of parameters among which the solution has to be found is limited to certain control requirements from which the general control requirements, valid for any chemical reaction, and special requirements determined from the analysis of the available experimental data and *a priori* kinetic information, have been isolated. The general control requirements are believed to include[17] the Law of Conservation of Matter, the Law of Conservation of Energy, and the requirement that the concentration of any reactant at any instant is non-negative. In essence, these requirements constitute a test of the validity of the formulation of the kinetic scheme and the validity of the integration of Eqns. (1). In conformity with the terminology developed in the present review, we shall refer to the control requirements as general if they differentiate a certain class of special kinetic models, within the framework of which the "true" model is located, and we shall call them special if they differentiate one special model from this class.

The general control requirements are formulated on the basis of data obtained or available outside the formal kinetic approach to the construction of mathematical models and qualitative information about the process investigated which the investigator usually processes. We shall consider, for example, the consecutive chemical reaction[127]

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C\,.$$

Suppose that the variation of the concentration of substance C, corresponding to the solution of special direct problems, is determined experimentally:

$$[C](t,\ k) = [A]^0[1 - \exp(-k_{\text{eff}}t)]. \tag{16}$$

In the absence of *a priori* information about the process mechanism, two special direct problems, defined by special control requirements, correspond to this solution: (1) $k_1 > k_2$ and (2) $k_1 \ll k_2$; accordingly, we have $k_{\text{eff}} = k_2$ or $k_{\text{eff}} = k_1$. The problem is formally outside the framework of the first level. In an informal consideration of A and B, the latter are real chemical substances and the possibility of the realisation of a particular special direct problem is determined in essence by the strength of the chemical bond in the corresponding molecules. Thus *a priori* information about the bond strength in the molecules of substances A and B makes it possible to formulate general control requirements within the framework of which the solution to the problem must be sought. For example, if the bond strength is greater in the molecule of substance A, then the general control requirement has the form $k_1 \ll k_2$. Analysis of semiquantitative data for the concentration of the intermediate B, which is not measured, leads to an analogous result. For example, when $\text{Max}[B](t) \ll [A]^0$, we obtain $k_1 \ll k_2$ and $k_{\text{eff}} = k_1$. The regions corresponding to the existence of different kinetic types of mechanisms of the liquid-phase oxidation reaction of hydrocarbons in the oxidation of hydrocarbons inhibited by phenol have been related[128,129] to the R–H bond strength and temperature. For these classes of reactions, it is possible to isolate, on the basis of the bond energy and temperature, the general control requirements within the framework of which the converse problem should be solved.

Qualitative information about the process investigated may include at least two kinds of data:[22] (1) semiquantitative data on the yield of particular reaction products or the concentrations of intermediate reactants; (2) data concerning any effect observed in the system, for example, critical phenomena, the effect of inhibiting or initiating additives, etc. Formal mathematical treatment of such data makes it possible to differentiate a system of general control requirements.

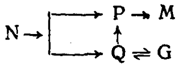
The question of the formal treatment of the control requirements ensuring the limitation of the region in which the converse problem is to be solved has been examined[14,22,26] but it is outside the framework of the present review. We shall only note that the control requirements must determine unambiguously the region in the rate constant space where the given special catalytic model of the process is realised.

Evidently the general control requirements unambiguously define the special kinetic model only for thoroughly investigated processes when a large amount of *a priori* physicochemical information is available. For example, such information has been obtained in the determination of the kinetics of the catalytic action of trinuclear clusters of the oxoacetates of the iron–chromium series in the model reaction involving the oxidation of ascorbic acid by hydrogen peroxide.[130] However the determination of such information is frequently associated, for example, in the study of pharmacokinetic reactions,[49] with serious experimental difficulties even for the example of consecutive chemical reactions considered above. Thus the problem of the identification of the kinetic type of the reaction mechanism—a converse second level problem—then comes to the fore.

VI. IDENTIFICATION OF THE REACTION MECHANISM

The ambiguity of the solution of the converse problem in terms of the traditional formulation is expressed, on the one hand, by the degeneracy of the minimum in the functional reflecting the similarity between the experimental and theoretical values of the observed variables, and, on the other hand, by the appearance of local minima in this functional. In both cases the ambiguity is caused by the deficiency of the experimental data, manifested in the asymptotic character of the system of differential Eqns.(1). Hitherto the formulation of the problem subject to the condition that the minimum in the functional is degenerate has been considered; we shall now deal with the formulation of problems involving the presence of local minima in the functional. The formulation of the converse problem as the problem of selecting the versions of the mechanisms agreeing well with the amount of experimental data arose as the natural response by investigators in the field of kinetics to the lack of validity of the traditional formulation.[33]

In the early studies the versions of the mechanism (the hypothesis about the mechanism) were special cases of a certain general kinetic scheme including all the process stages considered in the alternative versions of the mechanism.[13–15,26,57,101,102,131] For example, Peterson[131] considered eight alternative mechanisms of the oxidation of naphthalene and later Bard and Lapidus[50] considered thirteen such mechanisms, which are special cases of the general mechanism



where N is naphthalene, P phthalic anhydride, M maleic anhydride, Q naphthoquinone, and G gaseous products.

The need to formulate the problem by selecting the possible mechanism was dictated by the experimentally demonstrated lack of validity of the traditional formulation of the problem.[20,26] Indeed, if the formulation had been correct, then rate constants close to zero would have been obtained for stages which "do not occur" (the reactions take place at negligible rates) in the solution of the converse problems. However, even in the case of model problems[26] this was not found to be the case.

The presence of local minima in the functional in the case of mechanisms from which one cannot exclude any one stage necessitated an increase in the complexity of the concept of "version of the mechanism". Thus the ratios of the rates of individual stages[13,22] and different hypotheses concerning the reactivity of the intermediate reactants[20,22] have been included in this concept. It has been shown[22] that all these hypotheses are special cases of the description of experimental data by an asymptotic form of the complete system of differential Eqns.(1).

The need for the structural identification of kinetic models arises in the formal approach[20] to the study of any fairly complex process. Thus the model reaction involving the initiated chain consumption of a substance M with quadratic destruction of the active centre R, determined by the following kinetic scheme, has been considered:[22]

Stages	Pathways						
	I	II	III	IV	V	VI	VII
(1) $\xrightarrow{w_1} R$	1	2	0	1	2	0	0
(2) $M \rightarrow R$	1	0	2	1	0	2	0
(3) $R + M \rightarrow R + \Pi$	0	0	0	1	1	1	1
(4) $2R \rightarrow$ chain termination	1	1	1	1	1	1	0

If the experimental relation $[M]^{\exp}(t)$ is determined by a solution of the general direct problem with smaller dimensions, i.e.

$$\frac{d[M]}{dt} = -k_{eff}[M]; \quad [M](0) = [M]^0 ,$$

then the experimental data will be described by a kinetic model corresponding to pathway III:

$$\frac{d[M]}{dt} = -k_2[M]$$

and the model corresponding to cyclic pathway VII, where the concentration of active centres is determined by pathway II:

$$\frac{d[M]}{dt} = -\varkappa[M] ,$$

where $\kappa = k_3(w_1/k_4)^{1/2}$.

An analogous situation has already been considered above for the case of a consecutive chemical reaction.[127] The existence of several special kinetic models, describing equally well the experimental data, has been demonstrated, for example, in two investigations,[26,114] while the existence of local minima in the functionals, in which the quality of the description of the experimental data is different, has been described in other studies.[20,115,132]. Thus the need arises for a procedure whereby the local minima could be sorted and which would make it possible to find a unique solution to the problem of the identification of the reaction mechanism or which would demonstrate the non-unique nature of the solution.

As can be seen from the examples presented, local minima arise in the region of the rate constants space corresponding to different special kinetic models.[21] The hypothesis that, in the region where a particular kinetic type of reaction mechanism applies, local minima can exist enabled Pavlov and Brin[22] to reduce the problem of sorting the local minima to the problem of dividing the rate constant space into sections in which the system (1) has specific asymptotic properties. This creates the possibility of extending the approach, used in the selection of the possible process scheme,[13–15,26,50,102,131] to the problem of the identification of the kinetic type of reaction mechanism.[22,80] Thus the solution of the problem at this level (when the hypotheses Π_1–Π_3 are known) is determined by the following procedure:[80]

(1) The formal treatment of the qualitative data concerning the process in the form of a system of control requirements common to all the alternative hypothetical mechanisms.

(2) The formulation of hypotheses and specification of a system of special control requirements distinguishing one hypothesis from another (taking into account the possible change in the reaction regime).

(3) The selection for each hypothesis of the initial values of the rate constant ensuring the satisfaction of the control requirements (general and special) and a parametric test of the adequacy of the corresponding mathematical models.

(4) Statistical analysis of the results of tests of each hypothesis.

(5) Logical design of a discriminating experiment.

(6) The representation of the results of the solution of the problem.

Fairly extensive experience has now accumulated in the solution of problems in terms of such formulation. For example, this procedure has been used to select the most probable mechanism of the radiation-initiated isotope exchange between deuterium and the hydroxy-groups of silica gel,[26] to investigate the mechanism of the formation of methane in the pyrolysis of ethane,[133] to establish a possible mechanism of the oxidation of anthrahydroquinone by molecular oxygen,[122] to study the catalytic hydrogenation of phenol and the conversion of methane,[13] to model the kinetics of the liquid-phase oxidation of tetralin,[104] to identify the mechanism of the inhibited liquid-phase oxidation of hydrocarbons,[101,102] etc. In the main, hypothetical mechanisms differing in the set of elementary stages were considered in these investigations and the limiting transitions to systems of differential-algebraic equations were assumed to be known *a priori*.

The abundance of kinetic types of reaction mechanisms, which can be formally realised within the framework of a complex scheme, and the sometimes extremely large expenditure of computer time on the test of each hypothetical mechanism limit the scope of the approach. We shall list certain procedures which make it possible to overcome these difficulties and to facilitate and accelerate the solution.[22,80] Firstly, *a priori* information can be used to reduce the number of hypotheses considered. Secondly, it is possible to design and carry out an experiment whose aim is to compare qualitatively the principal observed kinetic features with the features obtained using various special kinetic models. For example, comparison of the experimental ratio of the initial rates of consumption of methylacrolein and the accumulation of methacrylic acid with the same ratio arising from different hypotheses about the reaction mechanism made it possible to eliminate a series of hypothesis from consideration.[80] Thirdly, one can design and carry out an experiment which makes possible the successive refining of the mechanism with increase of the amount of experimental material available. For example, this approach made it possible to analyse at each stage of the treatment not more than three hypothetical kinetic types of reaction mechanisms.[115]

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Thus, the study of converse problems can be recommended to experimenters as a method facilitating the complex procedure whereby one establishes the mechanisms of chemical reactions. By regarding the study of converse problems as a generalised kinetic approach to the construction of mathematical models, one can use such studies as a method for the investigation of the mechanisms of complex reactions.

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Application of the Spin Trapping Method in Kinetic Measurements

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The results obtained in recent years by the spin trapping method in the solution of a number of kinetic problems are analysed and a systematic account is given of the rate constants for the addition of alkyl, polychloroalkyl and hetero-radicals as well as certain others to nitroso-compounds and nitrones; the kinetic data obtained by the spin trapping method in the study of the isomerisation, fragmentation, elimination, substitution and addition reactions are surveyed.
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I. INTRODUCTION

The spin trapping (ST) method is used widely and successfully in the study of the mechanisms of reactions involving radicals.[1-16] Its essential feature consists in the fact that the short-lived radicals formed in the reaction add to the ST agent (STA) specially introduced into the reaction mixture, which leads to the formation of stable radicals capable of being identified by EPR.

The range of compounds which can be used as STA is fairly large. The present review includes the results obtained using nitroso-compounds and nitrones as STA.[1-10] When radicals are captured by these compounds, the products are mainly nitroxy-radicals, whose physicochemical properties have been thoroughly investigated.[17-19] The large set of such STA,[1-7] their selectivity,[5,20-23] and their other features[24-28] make it possible to identify radicals of different nature by EPR.

In order to identify the radicals formed during the reaction, it is essential to know the rate constants for their addition to the STA. These data are also required for the quantitative estimation of the rates of individual stages of complex chemical processes. The rate constants for the addition of a wide range of radicals to STA have now been determined and kinetic data characterising different stages of important processes in radical chemistry have been obtained. The present review is devoted to a survey of these results and an analysis of the scope of the ST method in the study of the reaction kinetics.

II. THE SPIN TRAPPING METHOD IN KINETICS

The radicals $\dot{R}_1$ formed in the reaction interact with the STA, giving rise to nitroxy-radicals—spin adducts (SA):

$$\dot{R}_1 + STA \xrightarrow{k_1} R_1R\dot{N}O \ . \qquad (1)$$

The radicals can participate in the following reactions:

(a) addition

$$\dot{R}_1 + M \xrightarrow{k_2} \dot{R}_2 \ , \qquad (2)$$

where M is the monomer,

(b) isomerisation

$$\dot{R}_1 \xrightarrow{k_3} \dot{R}_3 \ , \qquad (3)$$

(c) fragmentation or elimination

$$\dot{R}_1 \xrightarrow{k_4} X + \dot{R}_4 \ , \qquad (4)$$

(d) substitution

$$XR_5 + \dot{R}_1 \xrightarrow{k_5} \dot{R}_5 + R_1X \ . \qquad (5)$$

These reactions compete with the main reaction (1) if their rates are comparable to that of the latter.

The radicals $\dot{R}_i$, where i = 1–5, can recombine or disproportionate:

$$\dot{R}_i + \dot{R}_i \xrightarrow{k_6} \text{non-radical products.} \qquad (6)$$

The use of the ST method implies that the rate of capture of the radicals obtained in reactions (1)–(5) by the STA is higher than the rate of their conversion into non-radical products. The rate constants for the recombination and disproportionation of short-lived radicals are of the order of $k_6 \cong 10^6–10^{10}$ litre mol^{-1} s^{-1}.[29-35] If the concentration of the short-lived radicals $\dot{R}_i$, which depends on the rate of initiation of the reaction, does not exceed $10^{-7}–10^{-8}$ M and $[RNO]_0 \cong 10^{-2}–10^{-3}$ M (the STA concentrations most frequently used in experiments[1,5]), then it follows from the condition $k_i[RNO]_0 \gg 10^8–10^{10}\ [\dot{R}_i]$ that, when

$$k_i \gg 10^2 \div 10^6 \text{ litre mol}^{-1}\,\text{s}^{-1}, \qquad (7)$$

stage (6) can be neglected (k_i is the rate constant for the addition of the radicals $\dot{R}_i$ to the STA). Consequently if $[STA]_0 \cong 10^{-2}–10^{-3}$ M and condition (7) holds, it is possible to disregard stage (6). For example, it has been shown[30] that the recombination of alkyl radicals may be neglected when the solution contains 2×10^{-2} M 2,4,6-tri-t-butylnitrosobenzene.

Thus the knowledge of the rate constants for the addition of the radicals $\dot{R}_i$ to STA makes it possible to select initial STA concentrations and to create necessary experimental conditions such that it is possible to disregard the recombination and disproportionation of radicals and hence to simplify appreciably the reaction mechanism in kinetic studies.

The rate constants for the addition of the radicals $\dot{R}_i$ to STA (k_1) have been determined mainly using the methods of competition kinetics. Under these conditions, reactions (2) to (5), for which the rate constants k_i (i = 2–5) have been measured, were used as the reactions competing with the addition of the radicals $\dot{R}_1$ to STA. The rate constants k_1 have been determined using the methods of non-stationary kinetics $\{d[R_1R\dot{N}O]/dt \neq 0\}$ and quasi-stationary concentrations $\{d[R_iR\dot{N}O]/dt = 0\}$.

The difference between the ST method and the direct detection of the short-lived radicals in the liquid phase by EPR consists in the fact that the time required to obtain a stationary concentration of the nitroxy-radicals amounts in many cases to many minutes, which permits the measurement of the rate of formation of these radicals. Such experimental conditions are reached when STA effective in relation to the given radical at low rates of initiation are used. It has been demonstrated,[36] in particular, that, for a rate of initiation of 3×10^{-8} mol litre^{-1} s^{-1}, the times taken to attain a stationary concentration of the spin adducts (SA) of the $Cl_3\dot{C}$ radicals with 2-methyl-2-nitrosopropane (MNP) at $[MNP]_0 = 3.73 \times 10^{-3}$ M, nitrosodurene (ND) at $[ND]_0 = 3.27 \times 10^{-3}$ M, and α-phenyl-N-t-butylnitrone (PBN) at $[PBN]_0 = 2.15 \times 10^{-2}$ M are 7.5, 54, and 4 min respectively.

The formation of the nitroxy-radicals A and B is described by Scheme I when reaction (2) is used as one competing with the addition of the radicals $\dot{R}_1$ to the STA:

Scheme 1

$$\dot{R}_1 + RNO \xrightarrow{k_1} \underset{(A)}{R_1RN\dot{O}} \ ,$$

$$\dot{R}_1 + M \xrightarrow{k_2} \dot{R}_2 \ ,$$

$$\dot{R}_2 + RNO \xrightarrow{k_2'} \underset{(B)}{R_2RN\dot{O}} \ .$$

The rate constant k_1 is in this case determined by the expression

$$\frac{d[A]/dt}{d[B]/dt} = \frac{k_1[NRO]_0}{k_2[M]_0} = \frac{[A]}{[B]} \ , \tag{8}$$

where [A] and [B] are the concentrations of the STA radicals $\dot{R}_1$ and $\dot{R}_2$ before the attainment of their stationary values.

A method has been proposed[37] for the determination of k_1 on the basis of the measurements of the rate of formation of the radicals $R_1RN\dot{O}$ in the absence and presence of substances with which the radicals $\dot{R}_1$ can interact, for example, by adding to M via reaction (2). The constant k_1 is calculated from the formula

$$\frac{d[A]_{abs}}{d[A]_{pr}} = 1 + \frac{k_2[M]_0}{k_1[RNO]_0} \ , \tag{9}$$

where $d[A]_{abs}$ and $d[A]_{pr}$ are the increments of the concentrations of the SA of the radicals $\dot{R}_1$ with RNO in the absence and presence of M.

Eqns.(8) and (9) are valid under conditions where $d[\dot{R}_2]/dt = 0$ and $d[\dot{R}_1]/dt = 0$, which hold for short-lived radicals over a fairly short interval (see, for example, Denisov[38]). The choice of the STA is fairly wide. If the rate constant for the addition of the radical to one STA is known, then, by using the method of non-stationary kinetics, it is possible to determine the corresponding constants for other STA from the expression

$$\frac{[A]}{[B]} = \frac{k_1[RNO]_0}{k'[R'NO]_0} \ . \tag{10}$$

Eqn.(10) is valid for the reactions

$$\dot{R}_1 + RNO \xrightarrow{k_1} \underset{(A)}{R_1RN\dot{O}} \ ,$$

$$\dot{R}_1 + R'NO \xrightarrow{k'} \underset{(C)}{R_1R'N\dot{O}} \ .$$

When Eqns.(8) and (10) are employed, it is essential to know the relative stabilities of the nitroxy-radicals. It is known[17-19,35] that the stability of these radicals is determined by many factors. However, the relative stabilities of the radicals A and B or A and C, identified by EPR, can be estimated directly in the course of the study of the reaction. For this purpose, it is necessary to follow over a time interval the variation of the ratio of the concentrations of the radicals detected by EPR, and then to extrapolate this ratio to the start of the reaction.[39,40]

The nitroxy-radicals formed in the course of the reaction reach stationary concentrations in many instances after a short time interval. For this reason, the measurement of the rate of their formation involves considerable experimental difficulties. In the study of such reactions, the rate constants for the addition of the radicals $\dot{R}_1$ to the STA are determined by the method of quasi-stationary concentrations. The necessary and sufficient conditions for the determination of this constant after the attainment of stationary concentrations by the nitroxy-radicals will be examined in relation to the systems where reaction (2) competes with reaction (1). Such processes can be described by Scheme I supplemented by the recombination and disproportionation stages:

$$\left.\begin{array}{l} A + \dot{R}_1 \\ B + \dot{R}_1 \end{array}\right\} \xrightarrow{k_{11}} \text{non-radical products;} \tag{11}$$

$$\left.\begin{array}{l} A + \dot{R}_2 \\ B + \dot{R}_2 \end{array}\right\} \xrightarrow{k_{12}} \text{non-radical products;} \tag{12}$$

$$\left.\begin{array}{l} A + B \\ A + A \\ B + B \end{array}\right\} \xrightarrow{k_{13}} \text{non-radical products.} \tag{13}$$

If the conditions

$$k_{11}[\dot{R}_1],\ k_{12}[\dot{R}_2] \gg k_{13}([A]_{st} + [B]_{st}), \tag{14}$$

where $[A]_{st}$ and $[B]_{st}$ are the stationary concentrations of A and B, are satisfied, then the addition of the radicals $\dot{R}_1$ to M in the presence of RNO can be described by Scheme I and by reactions (11) and (12) (the methods of calculation of k_{11}, k_{12}, and k_{13} are described below).

At $\dot{R}_1$ and $\dot{R}_2$ concentrations of 10^{-8}–10^{-9} M and for $[A]_{st} + [B]_{st} < 10^{-5}$ M, conditions (14) for certain short-lived radicals are fulfilled, because it is known[41-44] that k_{11} and k_{12} are greater than k_{13} by 5–7 orders of magnitude.

When account is taken of stages (11) and (12), it follows from Scheme I that

$$\frac{[A]}{[B]} = \frac{k_1[\dot{R}_1]}{k_2'[\dot{R}_2]} \ . \tag{15}$$

On substituting the stationary concentration

$$[\dot{R}_2] = \frac{k_2[M]_0[\dot{R}_1]}{k_2'[RNO]_0 + k_{12}([A] + [B]} \ , \tag{16}$$

in Eqn.(15), we obtain

$$\frac{[A]}{[B]} = \frac{k_1[RNO]_0}{k_2[M]_0} + \frac{k_{12}([A] + [B])\,k_1}{k_2k_2'[M]_0} \tag{17}$$

or

$$k_1 = \frac{k_2k_2'[M]_0}{k_2'[RNO]_0 + k_{12}([A] + [B]))} \cdot \frac{[A]}{[B]} \ . \tag{18}$$

It follows from Eqn.(18) that, in order to determine the k_1 for the chemical reactions described by Scheme I and stages (11) and (12), it is essential not only to identify the nitroxy-radicals A and B by EPR but also to know k_{12} and the rate constants for the addition of the radicals $\dot{R}_1$ and $\dot{R}_2$ to the STA. Eqns.(17) and (18) are the most general for the calculation of the rate constants for the addition of the radicals $\dot{R}_1$ to the STA in the case of chemical processes described by Scheme I and stages (11) and (12) when the radicals A and B have attained stationary concentrations. It follows from Eqn.(18) that, when $k_2'[RNO]_0 \gg k_{12}\{[A] + [B]\}$, then a simple expression can be used to calculate k_1:

$$k_1 = k_2 \frac{[M]_0}{[RNO]_0} \cdot \frac{[A]}{[B]} \ . \qquad (19)$$

Eqn.(17) is valid also under the condition where $k_1 \gg k_2'$ and $k_1[RNO]_0 \gg k_{11}\{[A] + [B]\}$ (or $k_1 \gtrsim 10^7-10^8$ litre mol^{-1} s^{-1}), i.e. when the radicals $\dot{R}_1$ are much more reactive than the radicals $\dot{R}_2$ in the interaction with the STA. It is desirable that the condition $[A]/[B] \cong 1$ (taking into account the multiplicity of the signals in the EPR spectra of the spin-adducts of the radicals $\dot{R}_1$ and $\dot{R}_2$, on the one hand, and STA, on the other) should hold, although the content of the nitroxy-radicals in the reaction mixture can be determined over a fairly wide range of $[A]/[B]$ ratios by means of standard computer programs for the simulation of EPR spectra.[45] Using Eqns.(17) with known values of k_1, k_2, and k_2' and having determined the dependence of the ratio $[A]/[B]$ on $[RNO]_0/[M]_0$,[46] it is possible to calculate k_{12}.

Application of the method of quasi-stationary concentrations[31] to the radicals formed in the processes described by Scheme I and stages (11) and (12) yields

$$[A] + [B] = \frac{k_1[\dot{R}_1] + k_2'[\dot{R}_2]}{k_{11}[\dot{R}_1] + k_{12}[\dot{R}_2]}[RNO]_0 \ . \qquad (20)$$

When the conditions

$$k_1 = k_2' \text{ and } k_{11} = k_{12} \qquad (21)$$

hold, it follows from Eqn.(20) that

$$[A] + [B] = \frac{k_1}{k_{12}}[RNO]_0 \ . \qquad (22)$$

Taking into account Eqns.(21) and (22), we obtain from Eqn.(18)

$$k_1 = \frac{k_2[M]_0}{2[RNO]_0} \cdot \frac{[A]}{[B]} \ . \qquad (23)$$

Thus, when conditions (21) hold, Eqn.(23) can be used to calculate k_1.

Eqns.(8), (9), (17)–(19), and (23) have been obtained for examples where the reaction competing with reaction (1) involves the addition of $\dot{R}_1$ to M. Other expressions for the calculation of k_1 can be obtained by similar procedures having selected reactions (3)–(5) as the reactions competing with the addition of $\dot{R}_1$ to the STA. Joint examination of reactions (1) and (3) or (4) yields an expression for the calculation of k_1 similar to Eqns.(8), (9), (17)–(19) and (23) in which $[M]_0 = 1$, $k_2 = k_3$, or $k_2 = k_4$ $[B] = [R_3R\dot{N}O]$, or $[B] = [R_3RN\dot{O}]$ respectively. Similarly, when reactions (1) and (5) are considered jointly, one must replace $[M]_0$ by $[X\dot{R}_5]$ in the above expressions and $k_2 = k_5$ and $[B] = [R_5RN\dot{O}]$ must be adopted.

Thus the identification by EPR of the spin-adducts of the radicals $\dot{R}_1$ and $\dot{R}_i$ (where $i = 2-5$) with the STA and the knowledge of the constants k_i are necessary for the determination of the rate constant for the addition of the radicals $\dot{R}_1$ to the STA using the methods of non-stationary kinetics and quasi-stationary concentrations. If Eqn.(9) is used, then it is sufficient to identify the SA of the radicals $\dot{R}_1$ with the STA in order to determine k_1. Another feature which makes this method convenient is the fact that it can be applied also in cases where the radicals $\dot{R}_i$ ($i = 2-5$), formed as a result of the involvement of $\dot{R}_1$ in secondary reactions [see reactions (2)–(5)], are not trapped by the STA.

For reactions described by Scheme II, i.e.

Scheme II

$$\text{initiator} \xrightarrow{v_i} \dot{R}_1 \ ,$$
$$\dot{R}_1 + RNO \xrightarrow{k_1} R_1RN\dot{O} \ ,$$
$$\dot{R}_1 + R_1RN\dot{O} \xrightarrow{k_{11}} \text{non-radical products,}$$
$$2R_1RN\dot{O} \xrightarrow{k_{13}} \text{non-radical products,}$$

the following expression is valid:

$$\frac{k_1[RNO]_0 - k_{11}[R_1RN\dot{O}]_{st}}{k_1[RNO]_0 + k_{11}[R_1RN\dot{O}]_{st}} = \frac{k_{13}}{v_i}[R_1RN\dot{O}]^2_{st} . \qquad (24)$$

It has been suggested[42] that the following expressions be employed to determine k_1, k_{11}, and k_{13}:

$$\left(\frac{d[R_1RN\dot{O}]_{st}}{d[RNO]}\right)_{[RNO]\to 0} = \frac{k_1}{k_{11}} \ , \qquad (25)$$

$$([R_1RN\dot{O}])_{[RNO]\to\infty} = (v_i/k_{13})^{0.5} \ . \qquad (26)$$

The rate of initiation is determined by the method of measurement of the initial rate of formation of $R_1RN\dot{O}$.[42,47] Having determined k_1 by Eqn.(25), it is possible to calculate k_{11}. The knowledge of the constants k_{11} and k_{13} and v_i makes it possible, in its turn, to establish the limits of validity of condition (14) and $k_1[RNO]_0 \gg k_{13}[R_1RN\dot{O}]_{st}$ and hence the limits of the applicability of Eqn.(18) or (19) in the calculation of k_1. Since k_{11} may be determined also by other physicochemical methods,[48–51] the agreement between their values calculated by two independent methods can serve as a criterion of the correctness of the rate constants found for the addition of the radicals to the STA.

There exists a fairly wide range of methods for the determination of the rate constants for the addition of short-lived radicals to the STA, which may supplement one another in one form or other.

III. THE RATE CONSTANTS FOR THE ADDITION OF RADICALS TO SPIN TRAPPING AGENTS

1. The Rate Constants for the Addition of Carbon-Centred Radicals

Primary, secondary, and tertiary alkyl radicals are trapped by a large number of STA.[1,4–6,52,53] It is noteworthy that, when 2,4,6-$(Me_3C)_3C_6H_2NO$ (BNB) is used as the STA, the secondary radicals add both to the nitrogen atom, giving rise to nitroxy-radicals, and to the oxygen atom with formation of anilino-radicals.[54,55] Tertiary alkyl radicals add exclusively to the oxygen atom of the NO group in BNB.

Ingold and co-workers[41–43] determined the rate constants for the addition of primary and secondary alkyl radicals to a large number of STA using the cyclisation of $H_2C{=}CH(CH_2)_3\dot{C}H_2$ (I) to the radicals $\dot{C}H_2{-}\overline{CH(CH_2)_3C}H_2$ (II) and of $H_2C{=}CH(CH_2)_3\dot{C}HMe$ (III) to the radicals $\dot{C}H_2{-}\overline{CH(CH_2)_3C}HMe$ (IV). The authors[42,43] chose cyclisation as the reaction competing with the addition reaction in the determination of the rate constants for the addition of the radicals (I) and (III) to the STA. The rate constants for the cyclisation of the radicals (I) and (III) had been calculated earlier from the EPR spectra.[43,56] The rate constants determined in the above investigations[42,43] for the addition of the radicals to the STA are listed in Table 1, which also includes the rate constants for the addition of the radicals $Ph\dot{C}Me_2$ and $\dot{C}Me_3$ to STA, obtained by Doba et al.[37] and Maeda and Ingold.[43] Table 2 summarises the data on the rate constants for the addition of carbon-centred radicals with functional substituents. It follows from Tables 1 and 2 [cf., for example, No.4 in Table 2 with the data for the radicals (III) in Table 1] the replacement of the alkyl group or hydrogen at the C_β atom by other substituents does not entail an appreciable alteration of the rate constants for the addition of the secondary radicals to the STA.

Table 1. The rate constants ($10^{-5}\,k_1$, litre mol^{-1} s^{-1}) for the addition of alkyl radicals to STA.

No.	STA	Radical			
		$H_2C{=}CH(CH_2)_3\dot{C}H_2$*	$H_2C{=}CH(CH_2)_3\dot{C}HMe$**	$Ph\dot{C}Me_2$**	$Me_3\dot{C}$***
1	MNP	90.2	61	100	33
2	ND	407.0	406	110	2000
3	BNB	4.7	0.18****; 3.1*****	4.8*****	2.3*****
4	PMNB	—	—	—	1400
5	NB	—	—	—	2000
6	DMPO	25.8	42	1.9	—
7	MBN	31.3	13	12	—
8	PBN	1.33	0.68	0.0027; 10******	0.1
9	4-MeO-PBN	1.16	—	—	—
10	4-Me-PBN	1.24	—	—	—
11	4-CN-PBN	1.68	—	—	—
12	4-NO_2-PBN	2.88	—	—	—
13	$(MeO)_3$-PBN	0.18	—	—	—

Notation: MNP = 2-methyl-2-nitrosopropane, ND = nitrosodurene, BNB = 2,4,6-tri-t-butylnitrosobenzene, PMNB = pentamethylnitrosobenzene, NB = nitrosobenzene, DMPO = 5,5-dimethylpyrroline 1-oxide, MBN = methylene t-butyl nitrone, and PBN = α-phenyl N-t-butyl nitrone.

*At 40 °C.[42]
**At 40 °C.[43]
***At 26 °C.[37]
****Nitroxy-radical.
*****Anilino-radical.
******At 60 °C.[57]

Table 2. The rate constants for the addition to STA of carbon-centred radicals with functional group substituents.

No.	STA*	Radical	$10^{-5}\,k_1$, litre mol^{-1} s^{-1}**	Refs.
1	PMNB	cyclo-$\dot{C}_6H_{11}$	160 (26°)	[58]
2	MNP	$(Me_3Co)_2\dot{C}H$	9—45 (25°)	[59]
3	ND	$HO_2C(CH_2)_2\dot{C}H_2$	351 (40°)	[60]
4	ND	$CCl_3(CH_2CHMe)_n^{\cdot}$***	394 (40°)	[61]
5	$Me_2(COMe)CNO$	$RCH_2\dot{C}HCCl_2X$ ****	10 (60°)	[62]
6	PBN	$\dot{P}h$	120 (20°)	[63]
7	ND	$\dot{P}h$	30 000—60 000 (20°)	[64]

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*For the significance of the notation, see the footnote to Table 1.
**The temperature (in °C) at which k_1 has been determined is given in brackets.
***n = 1.2.
****X = Cl, F, or H.

2. The Rate Constants for the Addition of $\dot{C}Cl_3$ to Other α-Chloro-radicals

The range of STA which may be used for the identification of $\dot{C}Cl_3$ and other α-chlororadicals is limited.[5,21,65,66] The rate constants for the addition of chloro-radicals to the STA used most frequently for their trapping have been determined[36,67,68] (Table 3).

3. The Rate Constants for the Addition of Hetero-radicals

Table 4 presents the rate constants for the addition of hetero- and other radicals to the STA and also the rate constants for the addition of hydrogen and a hydrated electron.

Table 3. The rate constants for the addition of α-chloro-radicals to STA.

No.	STA*	Radical	$10^{-5}\,k_1$, litre mol^{-1} s^{-1}**	Refs.
1	ND	$Cl_3\dot{C}$	91 (20°)	[36]
2	ND	$Cl(CH_2)_2\dot{C}Cl_2$	13 (20°)	[36]
3	ND	$Cl_3CCH_2\dot{C}HCl$	14 (20°)	[68]
4	PBN	$Cl_3\dot{C}$	0.7 (20°)	[36]
5	MNP	$Cl_3\dot{C}$	18.9 (20°)	[36]
6	MNP	$Cl(CH_2)_2\dot{C}Cl_2$	1.7 (20°)	[36]
7	MNP	$Cl_3C\dot{C}HCl$	3.3 (40°)	[67]
8	MNP	$Cl_2HC\dot{C}Cl_2$	3.3 (40°)	[67]
9	MNP	$ClCH_2\dot{C}ClCCl_3$	3.8 (40°)	[67]
10	MNP	$ClCH_2CCl_2\dot{C}Cl_2$	3.8 (40°)	[67]

---

*For the significance of the notation, see the footnote to Table 1.
**The temperature (in °C) at which k_1 has been determined is given in brackets.

The radicals $Et_3\dot{S}i$ (V) are widely used for the generation of other radicals as a result of the abstraction of a halogen:

$$Et_3\dot{S}i + RHal \xrightarrow{k_{27}} Et_3SiHal + \dot{R}\ . \qquad (27)$$

The constants k_{27} for many halogen-containing compounds have been determined.[81] Various STA are used for the EPR identification of the radicals (V).[54,55,82,83] In the case of BNB, anilino-radicals are produced, while the reaction with PBN gives rise to nitroxy-radicals. The radicals (V) add at high rates to the carbonyl group in ketones:[82]

$$(V) + R'RCO \xrightarrow{k_{28}} R'R\dot{C}OSiEt_3\ . \qquad (28)$$

The constants k_{28} have been determined for certain ketones and the rate constants for the addition of the radicals (V) to BNB and PBN have also been determined[71,72] (see Table 4, Nos. 5 and 6). Reactions (27) and (28) have been adopted as the stages competing with the addition of the radicals (V) to the STA.

Table 5 lists the rate constants for the addition of the radicals $H\dot{O}$, $HO\dot{O}$, $\dot{C}H_2O$, $Me\dot{C}HOH$, $Me_2\dot{C}OH$, and $MeCH_2$.$\dot{C}HOH$ to substituted PBN.

It is seen from the data in Tables 1–5 that the rate constants for the addition to the most frequently used STA have been determined for a large number of radicals. Although these constants have been obtained in relation to different STA for some of the radicals, nevertheless by employing Eqn.(10) it is also possible to determine the rate constants for the addition of the radicals to other STA. The rate constants for the addition of the radicals to STA vary over a range of several orders of magnitude depending on the STA used. This property of the STA makes it possible to choose a suitable STA permitting the use of simpler expressions, for example Eqn.(19), for the determination of the rate constants for reactions (2)–(5).

It follows from Tables 1–3 that nitroso-compounds are more effective STA for the trapping of aliphatic carbon-centred and phenol radicals than nitrones. Among nitroso-compounds, aromatic compounds are more reactive than alkyl nitroxy-radicals, provided that there is no appreciable steric hindrance. The highest rate constants for the addition of radicals have been obtained for nitrosodurene (Tables 1 and 3, Nos.1–3). However, it does not follow from this that nitrosodurene is also the most reactive STA for other radicals, because the efficiency of the STA depends on many factors, for example on the stability of the SA formed,[84,85] on the thermal and photochemical stabilities of the STA, and other causes.

Table 4. The rate constants for the addition of hetero-radicals and other radicals to STA at 20 °C.

No.	STA	Radical	$10^{-5} k_1$, litre mol^{-1} s^{-1}	Refs.
1	4-Me-PBN	$H\dot{O}$	5 000	[69]
2	PBN	$PhCO\dot{O}$	1—100	[47, 63]
3	PBN	$Me\dot{O}$	1 200	[70]
4	PBN	$\dot{H}$	5 500	[30]
5	PBN	$Et_3\dot{S}i$	430—990	[71]
	PBN	»	60—120	[72]
6	BNB	$Et_3\dot{S}i$	16 000	[72]
7	DMPO	$H\dot{O}$	20 000—27 000	[69]
8	MNP	$Me\dot{O}$	1 300 (—40°)	[73]
9	MNP	$Ph\dot{S}$	1 700	[74]
10	PMNB	$Ph\dot{S}$	3 200	[74]
11	NB	$Ph\dot{S}$	2 200	[74]
12	DMPO	$Me_3C\dot{O}$	5 000	[75]
	DMPO	»	7 300	[76]
13	MNP	$Me_3C\dot{O}$	15	[75]
	MNP	»	11 (40°)	[77]
14	$H_2C{=}N(O)CMe_3$	$Me_3C\dot{O}$	3 000—5 000	[75]
15	HMPO	$Me_3C\dot{O}$	3 800	[76]
16	DeMPO	$Me_3C\dot{O}$	3 300	[76]
17	PMPO	$Me_3C\dot{O}$	4 100	[76]
18	Me_4-PO	$Me_3C\dot{O}$	86	[76]
19	PBN	e_{aq}	100 000	[78]
20	PBN	$CO_2^{\cdot}$	150	[78]
21	PBN	$CH_3\dot{O}$	120	[78]
22	PBN	$O_2^{\cdot}$	50	[78]
23	α-2-pyridine 1-oxide N-t-butyl	$H\dot{O}$	32 000	[79]
24	α-3-pyridine 1-oxide *N*-t-butyl nitrone	$H\dot{O}$	48 000	[79]
25	α-4-pyridine 1-oxide *N*-t-butyl nitrone	$H\dot{O}$	35 000	[79]
26	PBN	$Et\dot{O}$	2 000	[80]

Notation: 4-Me-PBN = 4-*N*-methylpyridine t-butyl nitrone, HMPO = 5-n-hexyl-5-methyl-1-pyrroline *N*-oxide, DeMPO = 5-n-decyl-5-methyl-1-pyrroline *N*-oxide, PMPO = 5-n-propyl-5-methyl-1-pyrroline *N*-oxide, and Me_4-PO = 3,3,5,5-tetramethyl-1-pyrroline *N*-oxide; for the significance of the remaining abbreviations, see the footnote to Table 1.

The high rate constants for the addition of carbon-centred radicals to aromatic sterically unhindered nitroso-compounds can be accounted for by the stabilisation of the SA as a result of the delocalisation of the unpaired electron over the aromatic ring,[86] so that aromatic alkyl hydroxy-radicals should be more stable than dialkyl nitroxy-radicals. However, comparison of the rate constants for the addition of thiyl radicals to NB, PMNB, and MNP (cf.Nos.9–11 in Table 4 and Nos.1, 4, and 5 in Table 1) shows that the efficiency of the STA can also involve factors other than the delocalisation of the unpaired electron in the SA.

In contrast to nitroso-compounds, aliphatic nitrones are more reactive than aromatic nitrones (Table 1, Nos.7–13; in addition, cf.No.14 in Table 4 with Nos.1–3, 5, and 6 in Table 5). It is believed[42] that this is associated, apart from other causes, with the steric factor, because aliphatic nitrones are less sterically hindered than aromatic nitrones. Comparison of the rate constants for the addition of certain radicals to substituted and unsubstituted nitroso-compounds and nitrones shows that the steric structure of the substituents influences significantly the reactivity of the STA (cf. Nos.2–4, 7, 8, and 13 in Table 1, Nos.14–18 in Table 4, and Nos.1–3, 5, and 6 in Table 5).

Table 5. The rate constants ($10^{-7} k_1$, litre mol^{-1} s^{-1}) for the addition of radicals to substituted α-phenyl n-t-butyl nitrones (PBN) at 25 °C.[78]

No.	STA	Radical						
		$Me_3C\dot{O}$*	$H\dot{O}$	$HO\dot{O}$	$\dot{C}H_2OH$	$Me\dot{C}HOH$	$Me_2\dot{C}OH$	$MeCH_2\dot{C}HOH$
1	PBN	0.55	850	0.5	4.3	1.6	1.0	1.3
2	4-Me-PBN	0.34	470	0.1	2.5	0.1	0.1	0.35
3	4-MeO-PBN	0.55	640	0.1	2.9	0.95	0.15	0.1
4	4-CN-PBN	—	650	0.6	75.0	2.0	—	1.7
5	4-NO_2-PBN	0.9	740	0.3	120.0	3.5	—	0.65
6	4-Cl-PBN	0.65	—	—	—	—	—	—

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*According to the data of Janzen and Evans;[75] the solvent was benzene, while in all the remaining cases it was water.

It follows from the data in Tables 4 and 5 that nitroso-compounds and nitrones are just as effective for the identification of oxygen-centred radicals. As for alkyl radicals, aliphatic nitrones are more reactive than aromatic nitrones (cf.No.14 and Table 1 and No.1 in Table 5). Furthermore, the polarity (Table 5) and steric properties (Nos.8–13 in Table 1 and Nos.15–18 in Table 4) influence appreciably the effectiveness of nitrones, as happens for aromatic nitroso-compounds (Table 1, Nos.2–4).

The causes of the differences between the activities of the STA in relation to different radicals are so far not altogether clear. For example, MNP is a relatively ineffective STA, compared with NB and PMNB, in the trapping of the Me_3C radicals (see Table 1, Nos.1, 4, and 5). However, it is seen from the comparison of the rate constants for the addition of thiyl radicals of MNP, NB, and PMNB (Table 4, Nos.9–11) that the difference between the effectiveness of these STA and that of thiyl radicals is insignificant. The strength of the bond between the radicals and the STA apparently has a significant influence on the effectiveness of the STA. Thus the rate constants for the addition of silicon-centred radicals to nitrones are somewhat higher (Table 4, No.5) than the corresponding rate constants for carbon-centred radicals (No.8 in Table 1 and No.4 in Table 3). On the other hand, the rate constants for the addition of silicon-centred radicals to BNB with formation of a silicon–carbon bond are greater by approximately two orders of magnitude than the rate constants for the addition of the same radicals to PBN (Table 4, Nos.5 and 6).

The rate constants for the addition of alkyl radicals of various types to the most effective STA have similar values (Table 1, Nos. 1–3 and 5; Table 2, Nos. 3 and 4). The radicals containing the HO group at the α-carbon atom are an exception (Table 5), which may be associated, apart from other causes, also with the fact that all these radicals have a planar or nearly planar structure[87,88] and the steric structure of the radicals identified does not therefore play a significant role.

The rate constants for chlorine-containing radicals depend appreciably on the nature of the radical. For example, the rate constants for the addition of the $Cl_3\dot{C}$ radicals to nitroso-compounds are approximately an order of magnitude greater than the corresponding rate constants for the $R\dot{C}Cl_2$ and $R\dot{C}HCl$ radicals (Table 3). This is probably associated with the geometry of the radicals, because it is known[87] that the $Cl_3\dot{C}$ radicals have a more pronounced pyramidal structure than the $R\dot{C}Cl_2$ or $R\dot{C}HCl$ radicals.

According to Ingold and co-workers,[42,43] the relative error in the determination of k_1 for aliphatic carbon-centred radicals is 30%. The error is determined mainly by the difficulty of measuring the relative stabilities of the radicals detected by EPR, because, during the initial period of the reaction, the signal to noise ratio precludes a more accurate determination of the relative SA concentration and the extrapolation of the ratio to zero time owing to the low concentration of the radicals. The absolute values of k_1 listed in Tables 1–5 can differ by a factor of 2–5,[42,43,59,77] which is associated with the accuracy of the determination of the rate constants k_i [i = 2–5, see reactions (2)–(5)] for other reactions competing with the addition of the radicals to the STA, because the k_i enter into the expressions for the determination of k_1 (see Section II).

Table 6 lists the activation energies and pre-exponential factors for the addition of n-alkyl radicals. It follows from these data that the pre-exponential factors are in the range characteristic of the addition of radicals to the double bond within the limits of the accuracy of their determination,[29,31,89,90] while the activation energy for this reaction is low.

Table 6. Parameters of the Arrhenius equation for the reaction involving the addition of radicals to STA.

STA*	Radical	T, °C	E, kcal mol^{-1}	log A (litre mol^{-1} s^{-1})	Refs.
MNP	n-alkyl	40—70	2.0	8.4	[42]
BNB	n-alkyl	40—73	1.0	6.5	[42]
PBN	n-alkyl	27—70	1.2	7.3	[42]
MNP	$CCl_3CH_2\dot{C}HCCl_2F$	—40—27	2.5	—	[62]

*For the significance of the notation, see the footnote to Table 1.

IV. THE USE OF THE SPIN TRAPPING METHOD FOR THE DETERMINATION OF THE KINETIC PARAMETERS OF ISOMERISATION, FRAGMENTATION, ELIMINATION, SUBSTITUTION, AND ADDITION REACTIONS

Section III listed the rate constants for the addition of short-lived radicals to STA. These constants were determined for cases where the reactions selected to compete with addition of the radicals $\dot{R}_1$ to the STA were cyclisation, substitution, or addition reactions whose rate constants were known. Certain data on the rate constants for the isomerisation, fragmentation, elimination, addition, and substitution of the radicals $\dot{R}_1$, obtained by the ST method, are compiled below. On the other hand, the addition of the radicals $\dot{R}_1$ to the STA for which the rate constant has been measured were selected as the reaction competing with the above reactions.

It has been shown in Section II that, in order to be able to determine the rate constants for reactions (2)–(5) by the ST method, it is essential to detect simultaneously by EPR the SA of the radicals $\dot{R}_1$ and $\dot{R}_i$ (i = 2–5) [except in the cases where it is possible to employ Eqn. (9)]. Evidently the STA whose SA with the radicals $\dot{R}_1$ and $\dot{R}_i$ have the simplest EPR spectrum are the most suitable for these purposes. Many nitrones satisfy this condition. On interaction of radicals with these compounds, fairly simple spectra are obtained, and the nitroxy-radicals formed are extremely stable. However, the spectra of the SA of many radicals with nitrones have similar hyperfine interaction (HFI) constants[24,91] and the lines due to individual radicals can therefore frequently overlap. Nevertheless, the large set of the possible nitrones[52,91,92] allows the elimination of these difficulties in many instances. As regards nitroso-compounds, their selection as the STA depends on many factors and therefore requires special study in the investigation of a particular reaction. Nitroso-compounds are known to be selective (see, for example, Freidlina et al.[5]) with respect to individual radicals. For this reason, it is not always possible to detect simultaneously the SA of the radicals $\dot{R}_1$ and $\dot{R}_i$ with the aid of nitroso-compounds. In such cases one can use Eqn. (9) to determine the rate constants for reactions (2)–(5).

When Eqns. (8), (9), (19), and (23) are used to determine k_2, it is necessary to know only the values of k_1. However, the application of these expressions requires that certain conditions be maintained. If these conditions are not fulfilled, then more complex expressions, for example Eqn. (17), may be used to determine k_2, which requires the knowledge of the rate constants for the addition of the radicals $\dot{R}_1$ and $\dot{R}_2$ to the STA. It follows from the data in Tables 1–5 that much information is now available about the rate constants for the addition of short-lived radicals to STA. The main difficulty with which the use of Eqn. (17) for the calculation of k_2 is associated consists in the comparatively small amount of data available for the rate constant k_{12}. However, on the basis of Eqns. (24)–(26), it is possible not only to determine k_{12} but also to establish the validity of condition (14).

1. Determination of the Rate Constants for the Isomerisation Reaction

The present development of the chemistry of radical processes has shown that the chemical processes involving the rearrangement of radicals in the liquid phase [see reaction (3)] are general and can be regarded as one of the principal types of radical reaction together with the fragmentation, elimination, substitution, and addition reactions.[35,90]

The rearrangements of radicals with 1,2-migration of the chlorine atom[93,94] and sulphur-containing groups[95] as well as different types of isomerisation with migration of hydrogen to a more remote radical centre[93,96] occupy an important place in the series of known rearrangements of short-lived radicals. Such rearrangements have been investigated by methods of preparative chemistry,[93–96], EPR,[21,66,67,97–101] and other physicochemical methods.[93,96,102,103]

The STA more effective in relation to the radicals $\dot{R}_1$ and $\dot{R}_2$ investigated, namely MNP and ND, have been used to determine the isomerisation rate constants k_3 (Nos.1 and 2 in Table 1 and Nos.7–10 in Table 3). The rate constants k_3 were determined with the aid of the expression

$$k_3 = k_1 [\mathrm{RNO}]_0 \frac{[\mathrm{R_3RN\dot{O}}]}{[\mathrm{R_1RN\dot{O}}]}$$

[see Eqn.(19)], which has been shown in Section II to be valid subject to the condition $k_3[\mathrm{RNO}]_0 \gg k\{[\mathrm{R_3RN\dot{O}}] + [\mathrm{R_1RN\dot{O}}]\}$, where k is the rate constant for the interaction of the radicals $\dot{R}_3$ with $\mathrm{R_1RN\dot{O}}$ and $\mathrm{R_3RN\dot{O}}$ [see reaction (12)].

(*a*) *Determination of the rate constant for the isomerisation of polyhalogeno-radicals with 1,2-migration of chlorine.* The attempts to determine the rate constant for the rearrangement of the radicals $\mathrm{CCl_3\dot{C}H_2}$ to $\mathrm{\dot{C}Cl_2CH_2Cl}$ with 1,2-migration of chlorine by the EPR method have been unsuccessful, because it has not been possible to observe signals due to the non-rearranged radicals even at −140 °C.[97,98] On the basis of the results obtained,[98] it has been suggested that these reactions are characterised by low activation energies and that the rate constant for the isomerisation of the primary radicals $\mathrm{CCl_3\dot{C}H_2}$ to $\mathrm{\dot{C}Cl_2CH_2Cl}$ is apparently $k_{is} \approx 10^{10}$ s^{-1} at 50 °C.[87,98]

Using the selectivity of nitroso-compounds, Freidlina et al.[5] detected the SA of the radical $\mathrm{CCl_3\dot{C}H_2}$ with $\mathrm{Me_2C(COMe)NO}$. The rearranged $\mathrm{\dot{C}Cl_2CH_2Cl}$ radicals have been detected with the aid of ND as the STA. In subsequent studies,[62,66,67] it was possible to detect simultaneously the SA of the non-rearranged and rearranged radicals in other reactions. These results made it possible to find an approach to the determination of the rate constants for the rearrangement of polyhalogeno-radicals with 1,2-migration of chlorine by the ST method.

The authors[62,66,67] used MNP as the STA for the determination of the rate constant for the isomerisation of polyhalogenoradicals with 1,2-migration of chlorine, because, with the aid of this compound, it is possible to establish the equivalence or non-equivalence of the two β-chlorine atoms in the SA of these radicals with the STA[66,104,105] and thereby assign unambiguously the spectra of the non-rearranged and rearranged radicals when these are present simultaneously in the reaction mixture (Table 7).

Table 7. Parameters of the Arrhenius equation for the reaction involving the isomerisation of the radicals $\dot{R}_1$ to $\dot{R}_3$.[39,60,62,66,67]

No.	$\dot{R}_1$	$\dot{R}_3$	$10^{-4} k_3$, s^{-1}	A, s^{-1}	E, kcal mol^{-1}
1	$\mathrm{CCl_3\dot{C}HCl}$	$\mathrm{\dot{C}Cl_2CCl_2H}$	1.8*	—	—
2	$\mathrm{ClCH_2\dot{C}ClCCl_3}$	$\mathrm{ClCH_2CCl_2\dot{C}Cl_2}$	1.0*	—	—
3	$\mathrm{RCH_2\dot{C}MeCCl_3}$	$\mathrm{RCH_2CMeCl\dot{C}Cl_2}$	3.3	10^{13}	12.5
4	$\mathrm{RCH_2\dot{C}HCCl_2F}$	$\mathrm{RCH_2CHCl\dot{C}ClF}$	10	10^{13}	10.5
5	$\mathrm{CCl_3\dot{C}H_2}$	$\mathrm{\dot{C}Cl_2CH_2Cl}$	10^3	10^{13}	8.0
6	$\mathrm{PhC(SPh)_2\dot{C}H_2}$	$\mathrm{Ph\dot{C}(SPh)CH_2SPh}$	5.6	$8 \cdot 10^{10}$	8.8
7	$\mathrm{RCO_2CH_2(CH_2)_3\dot{C}H_2}$	$\mathrm{RCO_2\dot{C}H(CH_2)_3Me}$	13	$3 \cdot 10^9$	6.3
8	$\mathrm{RCO_2CH_2(CH_2)_4\dot{C}H_2}$	$\mathrm{RCO_2\dot{C}H(CH_2)_4Me}$	1.8	$2 \cdot 10^{10}$	8.5
9	$\mathrm{RCO_2CH_2(CH_2)_2\dot{C}H_2}$	$\mathrm{RCO_2\dot{C}H(CH_2)_2Me}$	0.78	$7 \cdot 10^9$	8.6

*At 20 °C; in the remaining cases the data refer to 40 °C.

The rate constants for the isomerisation of certain polyhalogeno-radicals with 1,2-migration of chlorine determined in the above studies[62,66,67] and the parameters of the Arrhenius equation characterising these reactions are summarised in Table 7 (Nos.1–5). The knowledge of the isomerisation rate constants leads to the possibility of predicting a whole group of isotypical telomerisation, polymerisation, addition, and substitution reactions in which the intermediate radicals may rearrange with 1,2-migration of chlorine. In particular, the study of the polymerisation of $\mathrm{H_2C{=}CHCCl_2X}$, where X = Cl or F,[106] showed that the polymer formed consists mainly of the rearranged—$\mathrm{(CH_2.CHClCClX)}_n$—units. Since the rate of isomerisation of the secondary radicals is at least an order of magnitude higher than the rate of their addition to the monomer, the radicals $\mathrm{RCH_2\dot{C}HCCl_2X}$ formed have sufficient time to isomerise.

(*b*) *Determination of the rate constant for the isomerisation of the radicals $\mathrm{PhC(SPh)_2\dot{C}H_2}$ to $\mathrm{Ph\dot{C}(SPh)CH_2SPh}$ with 1,2-migration of the SPh group.* The rate constant for the rearrangement of the radicals $\mathrm{PhC(SPh)_2\dot{C}H_2}$ to $\mathrm{Ph\dot{C}(SPh).CH_2SPh}$ has been determined[39] in the temperature range 10–70 °C (Table 7, No.6). These radicals are obtained on thermal or photochemical isomerisation of acetophenone diphenylmercaptal to 1,2-di(phenylthio)ethylbenzene.[107] The activation energy and the pre-exponential factor obtained proved to be closer to the parameters characteristic of radical isomerisation[62,108,109] than to the parameters of the elimination[31,110] or addition[31] reactions. These results enabled the authors[39] to assume that the isomerisation of the radicals $\mathrm{PhC(SPh)_2\dot{C}H_2}$ to $\mathrm{Ph\dot{C}(SPh)CH_2SPh}$ with 1,2-migration of the thiyl group proceeds via an intramolecular mechanism.

(*c*) *Determination of the rate constant for the isomerisation of radicals with migration of hydrogen.* The SA of the initial $\mathrm{\dot{C}H_2(CH_2)_nCH_2CO_2R}$ and the rearranged $\mathrm{Me(CH_2)_n\dot{C}HCO_2R}$ radicals with ND have been identified by EPR.[60,101] The non-rearranged radicals were generated by abstracting bromine from $\mathrm{BrCH_2(CH_2)_nCH_2CO_2R}$ by triethylsilyl radicals.[101] The radicals $\mathrm{Me(CH_2)_n\dot{C}HCO_2R}$ are formed as a result of the rearrangement of the radicals $\mathrm{\dot{C}H_2(CH_2)_nCH_2.CO_2R}$ with 1,4-migration ($n = 2$), 1,5-migration ($n = 3$), and 1,6-migration ($n = 4$) of a hydrogen atom.

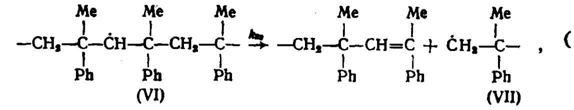
Table 7 (Nos.7–9) presents the temperature variation of the rate constants for the isomerisation of the radicals $\mathrm{\dot{C}H_2(CH_2)_nCH_2CO_2R}$ to $\mathrm{Me(CH_2)_n\dot{C}HCO_2R}$. These results were obtained over a narrow temperature range ($\Delta T = 30$ to 40 °C) and for a small number of experimental points.[101] Nevertheless it follows from the above data that 1,5-migration is preferred on both kinetic and thermodynamic grounds in reactions where there is a possibility of the rearrangement of the intermediate radicals with migration of hydrogen.

The use of the ST method yielded the kinetic and thermodynamic parameters for the isomerisation of short-lived radicals with migration of chlorine, the thiyl group, and hydrogen. The error in the measurement of the isomerisation rate constants, especially in the rearrangement of radicals with 1,2-migration of chlorine, is apparently half an order of magnitude and is associated with the inaccuracy in the determination of the rate constant for the addition of the non-rearranged radicals to the STA. Nevertheless the results obtained make it possible to take into account the role of the rearrangement stage in complex chemical reactions.

2. Determination of the Rate Constants for the Fragmentation Reaction

The rate constants for the fragmentation of the radicals $\mathrm{R\dot{C}O}$ (R = isopropyl, t-butyl, 1-adamentyl, tetra-allyl, and cumenyl) have been measured[57,77] using MNP as the STA.

The fragmentation of polymeric radicals via the mechanism



$$-CH_2-\underset{Ph}{\overset{Me}{C}}-\dot{C}H-\underset{Ph}{\overset{Me}{C}}-CH_2-\underset{Ph}{\overset{Me}{C}}- \xrightarrow{h\nu} -CH_2-\underset{Ph}{\overset{Me}{C}}-CH{=}\underset{Ph}{\overset{Me}{C}} + \dot{C}H_2-\underset{Ph}{\overset{Me}{C}}- , \quad (29)$$

(VI) (VII)

has also been studied.[111] Having determined the stationary concentrations (2g) of the SA of the radicals (VI) and (VII) with MNP and having adopted values in the range 3.3×10^6 to 9×10^6 litre mol^{-1} s^{-1} for the rate constants for the addition of the radicals (VI) to MNP, the authors[111] obtained $k_{29} = 5 \times 10^3 - 4.1 \times 10^4$ s^{-1} at 25 °C.

3. Determination of the Rate Constant for the Abstraction of a Chlorine Atom from CCl_4 by the Telomeric Radicals $CCl_3 . (CH_2CHX)_n^{\bullet}$ ($n = 1-3$; $X = H$, Me, or Cl) and Their Addition to Olefins

The telomerisation of the olefins $H_2C{=}CHX$ ($X = H$, Me, or Cl) with CCl_4 takes place at a fairly high concentration of the telogen via a radical chain mechanism:[112-114]

Scheme III

$$\text{initiator} \rightarrow \dot{R} \ ,$$

$$\dot{R} + CCl_4 \rightarrow RCl + \dot{C}Cl_3 \ ,$$

$$\dot{C}Cl_3 + H_2C{=}CHX \rightarrow CCl_3CH_2\dot{C}HX \ ,$$

$$CCl_3CH_2\dot{C}HX + H_2C{=}CHX \xrightarrow[(a)]{k_p^1} CCl_3CH_2CHXCH_2\dot{C}HX \ ,$$

$$CCl_3CH_2\dot{C}HX + CCl_4 \xleftrightarrow[(b)]{k'_{tr}} \underset{(T_1)}{CCl_3CH_2CHXCl} + \dot{C}Cl_3 \ ,$$

. . . .

$$CCl_3(CH_2CHX)_n^{\bullet} + H_2C{=}CHX \xrightarrow[(c)]{k_p^n} CCl_3(CH_2CHX)_{n+1}^{\bullet} \ ,$$

$$CCl_3(CH_2CHX)_n^{\bullet} + CCl_4 \xrightarrow[(d)]{k_{tr}^n} \underset{(T_n)}{CCl_3(CH_2CHX)_nCl} + \dot{C}Cl_3 \ ,$$

$$2\dot{C}Cl_3 \xrightarrow{k_9} \text{products} \ .$$

It is seen from this scheme that the relative yield of the telomer-homologue T_n is determined solely by the competition between the stages involving the substitution and addition of the radicals $CCl_3(CH_2CHX)_n^{\bullet}$ [stages (*a*)–(*d*)]. The methods of competitive kinetics made it possible to investigate the reactivity of the radicals. The determination of the partial chain transfer constants $C_n = k_{tr}^n/k_p^n$ is a widely used method for such estimates. An appreciable difference between C_1 and C_n ($n \geq 2$) has been observed in the telomerisation of styrene,[115] ethylene, propene, and vinyl chloride[116] with CCl_4. In order to elucidate the causes of the changes in the quantities C_n, it is essential to calculate k_{tr}^n or k_p^n and to establish thereby the contribution of stages (*c*) and (*d*) to the telomerisation of CCl_4 with olefins.

The rate constants for the abstraction of chlorine from CCl_4 by the radicals $CCl_3(CH_2CHX)_n^{\bullet}$ (where X = H, Me, or Cl) have been determined[61,68,117] by the ST method. The telomeric radicals were generated by the photochemical decomposition of $CCl_3(CH_2CHX)_nI$ in the presence of $Hg(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2$.[118] In the determination of the rate constant $k_5 = k_{tr}^n$ for the abstraction of chlorine from CCl_4 by the radicals $CCl_3(CH_2CHX)_n^{\bullet}$, the authors[61,68,117] used ND as the STA, which is most effective in relation to these radicals, and also the expression†

$$k_{tr}^n = k_5 = k_1 \frac{[ND]_0 [CCl_3N(\dot{O})Ar]}{[CCl_4]_0 [CCl_3(CH_2CHX)_n N(\dot{O})Ar]} \ .$$

In particular, it has been shown[68] that, when a more general expression is used [see Eqn.(18)] to determine k_{tr}^n, the same values of k_{tr}^n are obtained as in the case where the above formula was used. This is associated with the fact that, as numerous results show,[36,41,42,61,68,117] the rates of addition of the radicals $CCl_3(CH_2CHX)_n^{\bullet}$ to ND are much higher than the rate of reaction of these radicals with the SA. The values of k_{tr}^n determined in a number of studies[61,68,117] are listed in Table 8.

Table 8. The chain transfer (k_{tr}, litre mol^{-1} s^{-1}) and propagation (k_p, litre mol^{-1} s^{-1}) rate constants for telomeric radicals at 40 °C.

No.	Radical	$10^{-4}\,k_{tr}$	$10^{-3}\,k_p$	Refs.
1	$CCl_3CH_2\dot{C}H_2$	0,39	45	[117]
2	$CCl_3(CH_2CH_2)_2^{\bullet}$	9,0	30	[117]
3	$CCl_3(CH_2CH_2)_3^{\bullet}$	14.0	19	[117]
4	$CCl_3CH_2\dot{C}HMe$	1.4	8.8	[61]
5	$CCl_3(CH_2\dot{C}HMe)_2^{\bullet}$	20.8	4.2	[61]
6	$CCl_3CH_2\dot{C}HCl$	0.045	168	[68]
7	$CCl_3(CH_2CHCl)_2^{\bullet}$	0.176	98	[68[

Table 9. The rate constants k_5 for the abstraction of hydrogen by the radicals $\dot{P}h$ [122] and $Me\dot{O}$ [123] at 20 °C.

Reaction	$10^{-5}\,k_5$, litre mol^{-1} s^{-1}	Reaction	$10^{-5}\,k_5$, litre mol^{-1} s^{-1}
$\dot{P}h + MeOH$	1.4	$Me\dot{O}$ + glycerol	13
$\dot{P}h + MeCHOH$	2.3±0.1	$Me\dot{O} + MeOCH_2OMe$	19
$\dot{P}h + Me_2CHOH$	4.1±0.1	$Me\dot{O} + HCOOMe$	48
$Me\dot{O} + MeCH_2OH$	5.0	$Me\dot{O} + MeOCH_2OH$	34
$Me\dot{O}$ + ethylene glycol	6.2	$Me\dot{O}$ + n-pentane	1

Freidlina and co-workers[61,68,117] determined the chain propagation rate constant k_p^n [see Scheme III, stages (*a*) and (*c*)] listed in Table 8 from the values of k_{tr}^n obtained and the partial constants C_n for chain transfer in the telomerisation reactions of propene and vinyl chloride.[116,119-121] It follows from the data in Table 8 that (1) the reactivity of the radicals $CCl_3(CH_2CHX)_n^{\bullet}$ (X = H, Me, or Cl) in reactions with CCl_4 depends significantly on the position of the CCl_3 group relative to the radical centre and on the nature of the substituents at the α-carbon atom, (2) the differences between the values of C_n for the telomerisation of ethylene and propene with CCl_4 are associated mainly with the differences between the rate constants for the abstraction of chlorine from CCl_4 by the radicals $CCl_3CH_2\dot{C}HX$ and $CCl_3(CH_2CHX)_n^{\bullet}$, where $n \geq 2$ and X = Me or H, and (3) the changes in the C_n for the telomerisation of vinyl chloride with CCl_4 are associated with changes in both k_{tr}^n and k_p^n.

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†This expression is analogous to Eqn.(19) with $k_5 = k_2$; $[M]_0 = [CCl_4]_0$, $[A] = CCl_3(CH_2CHX)_nN(\dot{O})Ar$, and $[B] = CCl_3N(\dot{O})Ar$, where Ar = 2,3,5,6-Me_4C_6H.

4. Determination of the Rate Constants for the Abstraction of Hydrogen by the Radicals $\dot{Ph}$ and $Me\dot{O}$

The rate constants in the abstraction of hydrogen from methanol, ethanol, and isopropyl alcohol by phenyl radicals have been determined[122] using PBN as the STA (Table 9). Table 9 presents also the rate constants for the abstraction of hydrogen from various compounds by the radicals $Me\dot{O}$. These data were obtained on the assumption that the rate constant for the addition of the radicals $Me\dot{O}$ to PBN is 1.2×10^8 litre mol^{-1} s^{-1}.

5. Determination of the Rate Constants for the Addition of Radicals to Compounds Containing the $S{=}C\langle$ Groups

It is known[12,15,124,125] that compounds containing the $S{=}C\langle$ linkages can be used as STA. The stability of the radicals formed then depends significantly on a series of factors (for further details, see Scaiano and Ingold[12]). Using MNP and $(Me_3C)_2C=S$ as the STA, Scaiano and Ingold determined the rate constants for the addition of methyl radicals to $(Me_3C)_2C=S$. The SA of the radicals $\dot{Me}$ with MNP and $(Me_3C)C=S$ have been identified by EPR at −40 °C:

$$\dot{Me} + MNP \xrightarrow{k_{30}} \underset{(VIII)}{MeN(\dot{O})CMe_3}\,, \tag{30}$$

$$\dot{Me} + (Me_3C)_2C{=}S \xrightarrow{k_{31}} \underset{(IX)}{MeS\dot{C}(CMe_3)_2}\,. \tag{31}$$

The value $k_{30} = 1.5 \times 10^5$ litre mol^{-1} s^{-1} was adopted for the rate constant for the addition of the radicals $\dot{Me}$ to MNP at −40 °C on the basis of the data of Perkins and Roberts.[59,77] The rate constant $k_{31} = 1.1 \times 10^6$ litre mol^{-1} s^{-1} was determined by comparing the rates of formation of the SA of methyl radicals with MNP and $(Me_3)_2C=S$ using the known value of k_{30}. The results obtained showed that alkyl radicals add to compounds containing the $S=C\langle$ linkage at high rates. Thus the interaction of the radicals $\dot{Ph}$ with $S = C(OPh)CH_2Ph$ and $S = C(OPh)CHPh_2$ yields in addition to the radicals $PhS\dot{C}(OPh)CH_2Ph$ and $PhS\dot{C}(OPh)CHPh_2$, i.e.

$$\dot{Ph} + S{=}C(OPh)CH_2Ph \xrightarrow{k_{32}} PhS\dot{C}(OPh)CH_2Ph\,, \tag{32}$$

$$\dot{Ph} + S{=}C(OPh)CHPh_2 \xrightarrow{k_{33}} PhS\dot{C}(OPh)CHPh_2\,, \tag{33}$$

the radicals $S = C(OPh)\dot{C}HPh$ and $S = C(OPh)\dot{C}Ph_2$:

$$\dot{Ph} + S{=}C(OPh)CH_2Ph \xrightarrow{k_{34}} S{=}C(OPh)\dot{C}HPh\,, \tag{34}$$

$$\dot{Ph} + S{=}C(OPh)CHPh_2 \xrightarrow{k_{35}} S{=}C(OPh)\dot{C}Ph_2\,. \tag{35}$$

With $k_{34} = k_{35} = 5 \times 10^6$ litre mol^{-1} s^{-1}, the rate constants for the addition of phenyl radicals to $S = C(OPh)CH_2Ph$ and $S = C(OPh)CHPh_2$ at 45 °C were found[15] to be $k_{32} = 2.3 \times 10^6$ and $k_{33} = 2.7 \times 10^6$ litre mol^{-1} s^{-1} respectively. It is noteworthy that the values of k_{32} and k_{33} determined by the ST method are virtually identical with the corresponding constants calculated on the basis of the direct identification of the radicals $PhS\dot{C}(OPh)CH_2Ph$ and $PhS\dot{C}(OPh)CHPh_2$ by EPR.[15]

The phenylation of benzene has been investigated[63] by the ST method. Having adopted the value of 1.2×10^7 litre mol^{-1} s^{-1} for the rate constant for the addition of phenyl radicals to PBN at 25 °C in methanol, the authors[63] obtained the constant $k_{add} \approx 10^5$ litre mol^{-1} s^{-1} for the addition of phenyl radicals to benzene, which agrees well with the results of the phenylation of benzene by phenyl radicals obtained by Levy et al.[126] and Scaiano and Stewart[127] using other methods.

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Thus the experimental results considered in this review demonstrate the probable usefulness of the application of the ST method in the determination of kinetic data for individual stages of complex chemical reactions of various types. Although the amount of such data is at present small, nevertheless one may hope that further accumulation of experimental rate constants for the addition of radicals to STA as well as the analysis of the dependence of the rate constants for the addition reaction on the steric and polar properties of the radicals and on the nature of the STA will permit a considerable extension of the range of reactions for which kinetic data may be obtained.

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The Conformations of Polymethine Dyes

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The conformational features of polymethine dyes and related compounds are examined and the principal factors controlled by the conformational equilibrium are identified. The methods for the determination of the geometrical structures of polymethines are discussed. Special attention is devoted to a new method for the determination of their conformations—from the absorption spectra of dyes with two chromophores.

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I. INTRODUCTION

Polymethine dyes are a special class of organic compounds: they possess the unique ability to sensitise to visible light light-sensitive materials based on silver halides. The capacity of polymethine dyes for aggregation and adsorption on silver halides depends greatly on the steric structure of the cations of the dye itself.[1-3] In particular *cis–trans* isomerism has a pronounced and a by no means unambiguous influence on the effectiveness of the sensitisation.

Yet another field in which polymethine dyes are applied has been established in recent years—laser technology. Lasers based on these compounds generate radiation in the range 500–1250 nm. It has been established that the isomerisation of polymethine dyes plays an important role in the degradation of the photoexcitation energy, which ultimately affects the luminescence and generation properties of these dyes.[4,5]

Finally, polymethine dyes are a convenient model for the theory of the colour of organic compounds. Systematic investigation of the dependence of the colour of polymethines on their structure has made it possible to test a number of important postulates of this theory: the influence of the electronic symmetry of the chromophores, the intermolecular steric hindrance, and the presence of neutral solvents (solvatochromism) on the colour.[6] Furthermore, it has been shown that certain spectral anomalies of polymethine dyes are caused by the *cis–trans* isomerism.

However, despite the fact that the study of the conformational features of polymethine dyes is of both theoretical and practical importance, special reviews on this topic have not so far been published. Isolated non-systematic data may be found in the review of Sturmer and Heseltine.[1] X-Ray diffraction data for a series of cyanines are presented in Smith's review[7] and their photoisomerisation is considered in Kuz'min's review.[4]

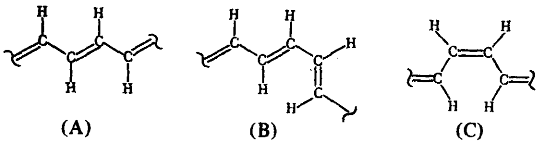
The aim of the present review is comparison of new and old spectroscopic data on the geometrical structure of polymethines and the elucidation of the factors on which it depends. Particular attention has been devoted to a new method for the determination of the conformations of polymethines—from the absorption spectra of dyes with two chromophores.

II. ROTATIONAL ISOMERISM OF COMPOUNDS RELATED TO POLYMETHINES

It is known that the ease of interconversion of atomic groups in the molecule depends on the order of the bond connecting these groups. For example, the barriers to the rotation of various substituted ethane derivatives are in the range 12–75 kJ mol^{-1}, while the barriers to rotation around significantly double bonds are extremely large (120–200 kJ mol^{-1}).[8] Hence, in contrast to the conformers of paraffins, the geometrical isomers of olefins are stable and can be isolated in a pure state. However, olefins tend to undergo photoisomerisation and the ratio of the products in the reaction mixture depends on the extinction coefficient of each isomer at the irradiation wavelength.[9]

The geometrical isomerism of polyenes can involve both double and single bonds. The planar *trans*-configuration (A) or the planar *s-cis*-configuration (B) and the *cis*-configuration (C) of the polyene chain are most energetically favoured; these configurations ensure the maximum interaction of neighbouring π-bonds, which can be represented by the following set of resonance forms:

$$-CH{=}CH-CH{=}CH- \longleftrightarrow -\overset{+}{C}H-CH{=}CH-\overset{-}{C}H- \longleftrightarrow -\overset{-}{C}H-CH{=}CH-\overset{+}{C}H-$$



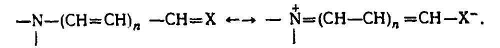
(A) (B) (C)

Since the contribution of ionic resonance structures should be small, polyenes are characterised by an appreciable alternation of bond orders. Even a slight shift of electron density is sufficient to increase the barrier to rotation about the central bond from 7.3 kJ mol^{-1} in but-1-ene[10] to 20.5 kJ mol^{-1} in butadiene.[8,10] One should also note that the *trans*-form of butadiene is more stable by 9.6 kJ mol^{-1} than the *s-cis*-form and that at room temperature butadiene exists in the most extended *trans*-form.

As a rule, the absorption bands in the UV spectra of *cis*-polyenes and the cyclised *s-cis*-dienes are less intense than the bands of the fully *trans*-isomers.[9,11] Yet another characteristic feature of the electronic spectra of *cis*-polyenes is the appreciable short-wavelength absorption—the so called "*cis*-peak".[9] The latter is completely absent from the spectra of *trans*-polyenes owing to the mutual cancellation of the components of the second transition moment, which are equal in magnitude, have opposite directions, and are oriented along the long chain of the molecule.[12] In order to account for the spectroscopic characteristics, it has also been suggested that the model involving the interaction of bound chromophores be used.[13,14] For this purpose, the polyene molecule is divided into two parts relative to the bond involved in the isomerism and each component is regarded as an autonomous chromophore. According to the theory of the interaction of bound chromophores,[13,15] any deviation of the torsional angle from 180° relative to the bond connecting the two chromophores removes the prohibition of the short-wavelength absorption.

Like olefins, polyenes undergo reversible *cis–trans* transitions under the influence of light.[9] Thus the *cis–trans* photoisomerisation constitutes the basis of the transformations of retinal, which play an important role in the visual process.[16]

Amides, thioamides, amidines, and their vinylene homologues can serve as examples of compounds with bonds more delocalised than those in polyenes. The electronic structure of these compounds is characterised by an appreciable contribution of the resonance dipolar structure (B):

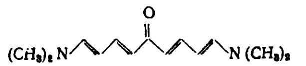


$$-\underset{|}{N}-(CH{=}CH)_n-CH{=}X \longleftrightarrow -\underset{|}{\overset{+}{N}}{=}(CH{-}CH)_n{=}CH{-}X^-.$$

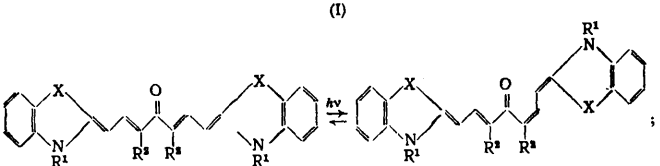
(A) (B)

Depending on the nature of the heteroatom X, the ease of the *s-cis–trans* isomerisation decreases in the sequence NR > O > S, which can be explained by the increased contribution of the structures (B) in the thione. The opposite variation has been found for the rotation about the remaining formally double bonds. For the vast majority of compounds of this kind (for $n > 0$), the isomerisation activation energy is in the range 38–96 kJ mol^{-1} and the acidity of the medium and the steric and the electronic structures of the substituents play a significant role. The relative thermodynamic stabilities of the conformers depend on the nature of the substituents and the dielectric properties of the medium.[8,17]

The ketocyanines (I) and (IIa), whose nature is similar to that of aminopolyvinyl ketones, have the fully *trans*-(*EEEEEEEE*)-structure:[18,19]†



(I)

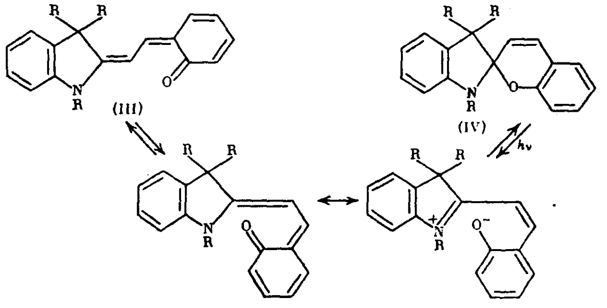


(IIa) (IIb)

$X{=}S,\ R^1{=}C_2H_5,\ R^2{=}(CH_2)_3;\ X{=}C(CH_3)_2,\ R^1{=}CH_3,\ R^2{=}H,\ (CH_2)_2,\ (CH_2)_3.$

In non-polar solvents the ketocyanines (IIa) undergo photoisomerisation with respect to a bond with a high order, the photoisomer (IIb) being stable and having a deeper but less intense colour compared with the initial form. The activation energy for the reverse reaction depends on the structure of the ketocyanine and also on the strength of the acid used as the catalytic additive and is in the range 41–71 kJ mol^{-1}.[20]

The merocyanines of type (III), formed as a result of the photoinitiated opening of the pyran ring of the spiropyran (IV), are a kind of analogue of aminopolyvinyl ketones:[21]

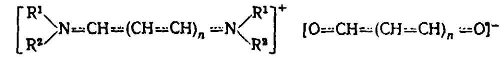


One of the stages in this reversible process is the *cis–trans* isomerisation with respect to the central bond, this stage determining the experimentally observed rate of the dark decolorisation.[22]

III. CONFORMATIONS OF VARIOUS POLYMETHINE DYES

1. Conformations of Streptocyanines

The protonation or alkylation of aminopolyvinylamines leads to the cationic conjugated systems (V)—streptocyanines, which possess "polymethine properties" i.e. their π bonds are fully delocalised and the charges on the atoms of the polymethine chain alternate.[23] The anionic systems (VI), namely oxanines, are also in the "polymethine state". The aminopolyvinyl ketones (thiones) in which the contribution by the dipolar limiting structure is comparable to that of the uncharged structure, i.e. merocyanines, are also close to the "polymethine state":

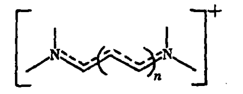


$$\left[{}^{R^1}_{R^2}\!\!>\!N{\,\overset{...}{=}\,}CH{\,\overset{...}{=}\,}(CH{\,\overset{...}{=}\,}CH)_n{\,\overset{...}{=}\,}N\!<^{R^1}_{R^2}\right]^+ \qquad [O{\,\overset{...}{=}\,}CH{\,\overset{...}{=}\,}(CH{\,\overset{...}{=}\,}CH)_n{\,\overset{...}{=}\,}O]^-.$$

(V) (VI)

Polymethine compounds are characterised by relatively narrow and intense principal absorption bands, which indicates a comparatively small change in bond lengths on excitation. A second maximum is usually observed on the short-wavelength side of these bands, being separated from the main maximum by 1200–1400 cm^{-1}. It is associated with the vibrational 0–1 transition polarised, like the 0–0 transition, along the axis of the polymethine chain.[24,25]

X-Ray diffraction data have shown that, regardless of the length of the unsubstituted polymethine chain and the presence of substituents at the nitrogen atoms, the cations of the streptocyanines have the fully *trans*-(E_{2n})-conformation with the equalisation of bond lengths characteristic of the "polymethine state" and a slight alternation of the valence angles formed by the sp^2-hybridised carbon atoms:[26–31]



The cations of the streptocyanines investigated are almost planar, which ensures the maximum interaction of the π-electrons and their delocalisation.

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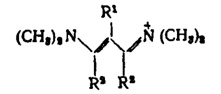
† Since different names are used to designate the same conformers of polymethines and related compounds, whenever necessary in the present review the two most frequently employed terms are used for them.

The ^{1}H NMR spectra[32-36] also support the fully *trans*-conformations of compounds (V) and (VI) in solution: the spin–spin coupling constants of the protons of the polymethine chain (12–14 Hz) do not change significantly also after the introduction of the bulky methyl group in the *meso*-position in the polymethine chain of the streptocyanine (V, n = 2), which rules out the formation of the *EZEE*-confirmation as a means of eliminating the steric hindrance which has arisen.

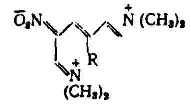
A narrow singlet in the ^{1}H NMR spectrum of compound (V, $n = 2$, $R^1 = CH_3$, $R^2 = C_6H_5$), due to aromatic protons, shows that the phenyl groups are arranged at right angles to the plane of the polymethine chain.[33]

The steric structure of the streptocyanines (VIIa, b) has been investigated with the aid of the nuclear Overhauser effect.[37] It has been shown that α,α′-di- and β-mono-alkylated trimethine streptocyanines exist in the fully *trans*-(*EE*)-conformation. Compared with the unsubstituted cation, there is some change in the valence angles, which is greater the greater the bulk of the substituent. The distortions of the angles and the deviation of the components of the cation from planarity for equal bulk of the substituent are greater in the α-derivatives (VIIa):



(VII)

$R^1 = H$, $R^2 = H, CH_3, C_2H_5$, iso-C_3H_7 (a); $R^1 = CH_3, C_2H_5$, iso-C_3H_7, t-C_4H_9, $R^2 = H$ (b)



(VIII)

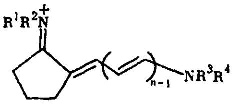
R=H (a); R=NO_2 (b)

Alkyl groups manifest weak electron-donating properties and their influence on the geometrical structure of the polymethines can be explained primarily by steric causes. Substituents such as the nitro-group are capable of being included in the conjugation chain, forming new chromophores and altering therby the conformation of the cation [compounds (VIIIa, b)].[38]

The ^{1}H NMR spectra of the streptocyanines (V, $R^1 = R^2 = CH_3$, n = 1, 2) exhibit two signals due to the protons of the methyl group at room temperature and for n = 3 also at a reduced temperature. The magnetic non-equivalence of these protons is caused by the hindered rotation of the methyl groups about the $\text{C}\cdots\text{N(CH}_3)_2$ bonds. With increase of the length of the polymethine chain, the barrier to rotation diminishes from 70 kJ mol^{-1} (n = 1) to 47 kJ mol^{-1} (n = 3). An increase in the acidity of the medium reduces the activation energy for the first compound to 36 kJ mol^{-1}. Experimental results[39,40] agree with data obtained by the *ab initio* calculation of the activation energies for the rotation of the amino-groups.[41]

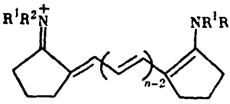
The electronic spectra of streptocyanines (V) cannot serve as a reliable criterion of their conformational homogeneity at room temperature, because instances of the overlap of the bands of isomers absorbing at close wavelengths are possible. A decrease of temperature as a rule causes a narrowing of the absorption bands as a result of the decrease of the amplitudes of low-frequency vibrations.[42] The appearance of inflections on the long-wavelength slopes of the principal bands was noted under these conditions [compounds (V), n = 2, 2, $R^1 = R^2 = (CH_2)_{3-5}$].[43] The authors[43] attribute such local maxima to the thermodynamically less stable mono-*cis*-conformers. The absorption bands of streptocyanines with shorter (n = 0, 1) chains do not inhibit such splitting. Apart from the principal long-wavelength band, the spectrum of compound (V, n = 3) shows yet another specific band in the region of shorter wavelengths, whose intensity increases on heating. By analogy with the short-wavelength absorption of *cis*-polyenes, this band has been called the "*cis*-peak" and has been assigned to absorption by the unstable *cis*-conformers, whose concentration in the equilibrium mixture increases with increase of temperature.

The fixation of the polymethine chain of streptocyanines in the mono-*cis*-($ZE_{2n-2}E$)-configuration (IX) and the di-*cis*-($ZE_{2n-2}Z$)-configuration (X) also leads to a bathochromic shift of the principal absorption band. Although the electronic influence of the substituent (the cyclic trimethylene group) also contributes to the magnitude of this shift, it is believed[44] that the contribution amounts to only half of the overall shift. The oscillator strength of the principal absorption band decreases in the sequence *trans* > *cis* > di-*cis*. The experimental results have been confirmed by LCAO-MO calculations.[44] Unfortunately the authors[44] did not pay attention to the short-wavelength part of the spectrum, where the appearance of "*cis*-peaks" on passing from the *trans*- to the *cis*-form might have been expected:



(IX)

$R^1, R^2 = CH_3, (CH_2)_4$; $R^3, R^4 = CH_3, C_6H_5, (CH_2)_4$

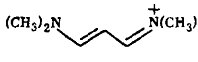


(X)

$R^1, R^2 = CH_3, (CH_2)_4$

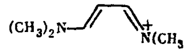
Characteristic changes in the absorption spectra of streptocyanines occur when their solutions are irradiated at the wavelength of the absorption maxima.[43,45-49] It has been established that this entails the appearance of a new band, which is displaced to longer wavelengths relative to the first and is characterised by a smaller oscillator strength. In many instances the appearance and increase of the intensity of the new band are accompanied also by the appearance and increase of the intensity of the bands of the "*cis*-peaks" polarised at right angles to the principal band.[43,45] The photochemical reaction is reversible and the rate of the dark reaction increases with increase of temperature and depends on the viscosity of the solvent. The process activation energies are in the range 58–67 kJ mol^{-1}. An increase of the acidity of the medium lowers this energy to 42 kJ mol^{-1}.[48] These spectroscopic data can be readily interpreted within the framework of the *cis*–*trans* isomerisation of streptocyanines, although the formation of the excimers of these compounds on excitation has been postulated.[43] However, photoisomerisation is supported by the activation energy, which is intermediate between the barriers to rotation about the double and single bonds, which corresponds to a bond order of 1.5 in the "polymethine state".

The phototropic mono-*cis*-(*EZ*)-form (XI) of the streptocyanine (V, $n = 1$, $R^1 = R^2 = CH_3$) has been compared with the di-*cis*-(*ZZ*)-form (XII), which is known to be stereohomogeneous.[43,46]



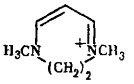
(V)

$\nu_{max} = 31750$ cm^{-1}
$f = 0.63$



(XI)

$\nu_{max} = 29400$ cm^{-1}
$f = 0.47$

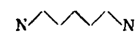


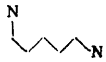
(XII)

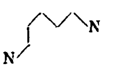
$\nu_{max} = 28400$ cm^{-1}
$f = 0.27$

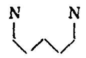
A distinct bathochromic shift and a decrease of the oscillator strength are observed on passing from the *trans*- to the di-*cis*-form.

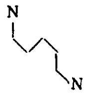
The same behaviour is reflected qualitatively by the results of the LCAO-MO calculation for certain conformers of pentamethine streptocyanine.[50] According to the calculated data, the energy of the ground state of the conformer increases in the sequence (A)–(F) and the bathochromic shift of the absorption band should take place in approximately the same order:

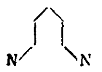

(A), fully *trans*-


(B), mono-*cis*-


(C), mono-*cis*-


(D), di-*cis*-

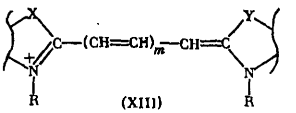

(E), di-*cis*-


(F), di-*cis*-

Calculation has also shown that the rotation around the central bonds of pentamethine streptocyanine requires the expenditure of 61 kJ mol^{-1}, while the rotation about the remaining C$\overset{\cdots\cdots}{-\!-\!-}$C bonds requires 58 kJ mol^{-1},[43] which is in fair agreement with experimental data.

2. Conformations of Monomethine Cyanines

True cyanines of type (XIII) differ from streptocyanines by the fact that the terminal nitrogen atoms, adjoining the polymethine chain, are at the same time components of heterocyclic nuclei.

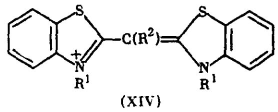

(XIII)

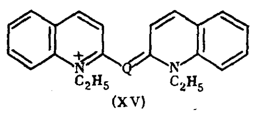
X, Y = O, S, $C(CH_3)_2$, CH=CH, NR; R = H, Alk, Ar

The closest methine group is also incorporated in the heterocyclic ring, so that the cyanine with m vinyl group corresponds to the streptocyanine with $n = m + 1$ vinyl groups.

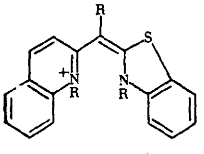
On passing from simple cyanines to compound (XIII), i.e. on replacement of a hydrogen atom by a bulky group X or Y, the steric interaction of the cation intensifies in the first place and the possibility of twisting about the C$\overset{\cdots\cdots}{-\!-\!-}$N bond vanishes in the second place. Furthermore, in asymmetric cyanines (X ≠ Y) the "polymethine state" differs from the ideal state, namely an alternation of bond orders arises and is more pronounced the greater the difference between the basicities of the terminal heterocycles.[51] The latter factor merits attention because a decrease of the order of a bond facilitates rotation about the latter.

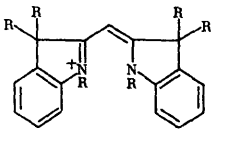
The steric interaction of the heterocyclic nuclei with one another is especially characteristic of monomethine cyanines (XIII, $m = 0$). According to X-ray diffraction data, the steric structure of the cations of monomethine cyanines depends primarily on the effective bulk of the groups X and Y in the terminal heterocycles and also on the presence of a substituent at the carbon atom linking these groups.[52-58] Thus the chromophores of monomethine cyanines (XIV, $R^1 = CH_3$, C_2H_5, $R^2 = H$) have the almost planar fully *trans*-(*EE*)-structure.[52,53] The same conformation obtains in the cation (XV, Q = CH), but, owing to the steric interaction of the hydrogen atoms in the 3 and 3′-positions, the planar structure is distorted (the central torsional angle increases to 50°). The angles between the planes of the heterocyclic rings and the C(2)C(9)C(2′) plane are the same.[54] On the other hand, the angles of rotation of the heterocyclic nuclei relative to the C(2)PC(2′) plane in the phosphorus-containing analogue (XV, Q = P), which also has the *trans*-(*EE*)-structure, are 40° and 24°, which means that the positive charge is displaced towards the first nucleus; this is also indicated by the proximity of the anion to it.[55]

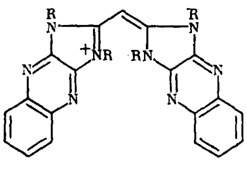

(XIV)


(XV)

The appearance of a bulky substituent at the *meso*-carbon atom precludes the formation of a planar structure of the cation owing to the strong steric hindrance. Furthermore, the most favourable form in which the cations of the *meso*-methylthiaquinocyanine (XVI) exist in the crystal is the di-cisoid form, in which the angle between the planes of the heterocycles is 60°.[56]


(XVI), $R = CH_3$

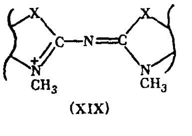

(XVII), $R = CH_3$

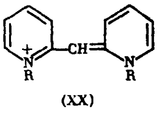

(XVIII), $R = C_2H_5$

The strong steric interactions of the isopropylidene groups in the hypothetical *trans*-form of monomethine indocyanine are the cause of the non-planar di-*cis*-(*ZZ*)-structure of the cation (XVII). The dihedral angle between the planes of the indolenine rings is 48°.[57]

The monomethine cyanines (XVIII) with terminal 1,1′,3,3′-tetraethylimidazo[4,5-*b*]-quinoxalinium nuclei, which are at an angle of 55°, also belong to non-planar dyes. In view of the high symmetry of the cation, all its conformations are degenerate.[58]

The number of signals of the *N*-alkyl groups can serve as a criterion for the selection of a particular conformation on the basis of ^{1}H NMR spectra. Thus a single signal due to *N*-methyl groups has been detected in the ^{1}H NMR spectra of monomethine quino-, oxa-, and thia-cyanines, which demonstrates, according to the author,[59] the *trans*-(*EE*)-configuration of these compounds. The introduction of a bulky alkyl substituent at the *meso*-carbon atom entails the splitting of this peak, which indicates the mono-*cis*-(*ZE*)-structure of the *meso*-substituted monomethine cyanines in solution. A similar splitting has been observed[59] for the aza-cyanines (XIX) and also for monomethine pyridocyanine (XX, $R = CH_3$). The simple structure of the ^{1}H NMR spectra in the regions corresponding to the resonance of the protons of the ethyl group and also comparison of the observed and calculated "aromatic" components of the spectrum permit the conclusion that compound (XX, $R = C_2H_5$) and its meso-analogue exist exclusively in the *trans*-(*EE*)-form:[60]


(XIX)


(XX)

The influence of the steric structure of substituents on the principal characteristics of the absorption spectra of monomethine cyanines has been observed in a number of studies.[2,61,62] It was found that the sterically unhindered monomethine thiacyanines (XIV, $R^1 = H$, $R^2 = H$ or CH_3; $R^1 = CH_3$, $R^2 = H$) have approximately the same absorption maximum at 425 nm, while the steric interactions in the sterically hindered dyes (XIV, $R^1 = R^2 = CH_3$) lead to an appreciable bathochromic shift of the band. The same pattern has been observed for a series of quinoline dyes. The possibility of the existence of various conformations of the sterically hindered dications has been postulated, but the spectroscopic shifts have been accounted for exclusively by a greater or lesser deviation of the components of the cation from the planar disposition.[2,61]

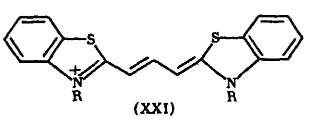
In contrast to this, Scheibe et al.[62] attribute all the spectroscopic changes for a series of monomethine pyrido- and quinocyanines exclusively to transitions to particular conformations. The choice of the geometrical structure of the cations in the above study[62] was based on the oscillator strength. The authors[62] justly assume that, by analogy with streptocyanines, the absorption intensity decreases in the series of structures *trans* > *cis* > di-*cis*. However, they compared dyes which differ both in their electronic structure and in the influence of substituents, on the one hand, and in their tendency towards solvation, on the other. Nor has any account been taken of the fact that the decrease of the absorption intensity can result not only from a *trans*–*cis* transition but also on distortion of the planar structure of the polymethine chain.

The study of the absorption bands of monomethine cyanines has shown that, in assigning the postulated conformers, one should take into account the short-wavelength part of the spectrum, since the presence of the "*cis*-peaks" can serve as proof of the presence of *cis*-forms. However, this procedure requires careful selection of the objects of comparison.[45,63] It has been noted[45,64] that monomethine cyanines do not undergo a photoisomerisation resembling that of streptocyanines or such photoisomerisation takes place with an extremely low quantum yield.

3. The Conformations of Carbocyanines and Their Vinylene Analogues

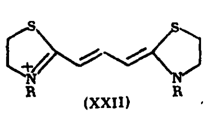
The carbocyanines (XIII, $m = 1$) are pentamethine streptocyanines as regards the length of the polymethine chain and differ from the monomethine cyanines in that the conformational transitions in their cations can take place via both the central and peripheral bonds of the polymethine chain.

X-Ray diffraction analysis of the thiacarbocyanines (XXI) unsubstituted in the polymethine chain has shown that their cations have exclusively the fully *trans*-(*EEEE*)-structure and are almost planar. According to different data, the dihedral angles between the planes of the heterocyclic nuclei and the plane of the remaining atoms of the chromophore range from 3° to 12°.[65–69] These angles depend on the effective bulk of the *N*-alkyl groups. Thus the replacement of an ethyl group by a methyl group leads to an appreciable flattening of the cation.[67–68] The *EEEE*-conformation of the chromophore is also realised in the crystal of thiazolinocarbocyanine (XXII). The polymethine chain and one of the heterocyclic nuclei then have a planar structure, while the second nucleus has the half-chair form.[70]



(XXI)

R = CH$_3$, C$_2$H$_5$

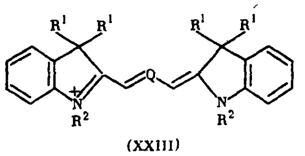


(XXII)

R = C$_2$H$_5$

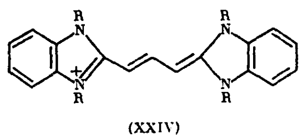
The indocarbocyanine (XXIIIa, Q = CH) also has a transoid structure in the crystal. The dihedral angle between the planes of the indoline nuclei is 13.8°. In the aza-analogue (XXIIIa, Q = N), this angle is 13.3°, while in compound (XXIIIa, Q = P) it amounts to 15.1°. In another crystalline modification, formed by the dyes (XXIIIa, Q = P or As), this angle diminishes to 6.8° and 6.3° respectively.[71]

The deviation of the planes of the heterocyclic nuclei in the crystal of imidocarbocyanine (XXIV) by 8° from one another is caused by the weak steric interaction of the ethyl groups.[72]



(XXIII)

R^1, R^2 = CH$_3$ (a); R^1 = CH$_3$, R^2 = C$_2$H$_5$ (b)



(XXIV)

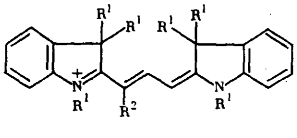
R = C$_2$H$_5$

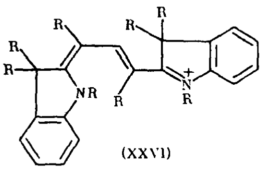
^{1}H NMR data for unsubstituted carbocyanines rule out the mono-*cis*-conformation with respect to the central bond, because the spin–spin coupling constant for the protons of the polymethine chain is 12–14 Hz and the mono-*cis*-conformation with respect to the peripheral bonds is ruled out owing to the equivalence of the *N*-alkyl groups.[73–75] The study of the indocarbocyanines (XXIIIb, Q = CH, N, or P) with the aid of the nuclear Overhauser effect has made it possible to rule out also the symmetrical di-*cis*-(*EZZE*)-form of these compounds.[76]

The conformational homogeneity of the unsubstituted thiacarbocyanines has been confirmed also by the fact that their absorption,[77–79] emission, and fluorescence excitation[79] spectra, recorded at room temperature, are virtually identical with the spectra obtained at a low temperature.

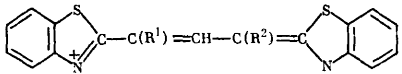
The pulsed photoexcitation of the cations of sterically unhindered carbocyanines leads to the appearance of short-lived *cis*-isomers, whose absorption bands have undergone a bathochromic (oxacarbocyanines) or hypsochromic (thiacarbocyanines) shift relative to the parent bands.[4,48,77,80–83] The activation energy for the reverse dark reaction is 50 kJ mol^{-1} for oxacarbocyanine and 63 kJ mol^{-1} for thiacarbocyanine.[64] The introduction of electron-donating substituents in the 6,6′-positions in the benzothiazole rings increases the activation energy, while the introduction of electron-accepting substituents diminishes it. This finding has been explained by the corresponding increase or decrease of the bond orders in the polymethine chain; here it is assumed that the photoisomerisation of carbocyanines unsubstituted in the polymethine chain involves the peripheral 2- and 8-positions.[82] In the photoisomerisation of asymmetric dyes, the activation energy for the *cis* → *trans* relaxation decreases with increase of the difference between the basicities of the terminal heterocycles. Since this is accompanied simultaneously by an enhancement of the alternation of bond orders in the polymethine chain, it is assumed[83] that the dark isomerisation involves a bond with a reduced order, i.e. takes place outside the more basic nucleus.

The introduction of a substituent in the α-position in the polymethine chain of the carbocyanine leads to a steric interaction of the substituent with fragments of the heterocyclic nucleus and the polymethine chain. In the crystals of α-ethylindocarbocyanine (XXV), the energy of such interaction is insufficient for the isomerisation of the cation and the latter therefore exists in a distorted fully *trans*-(*EEEE*)-conformation. The presence of a second substituent in the α′-position precludes the existence of the fully *trans*-form, probably owing to the steric interaction of the substituents, while the crystal of the cation (XXVI) exists in the di-*cis*-(*ZZEE*)-form, the dihedral angle between the planes of the heterocyclic nuclei amounting to 34.7°.[84]


(XXV)
$R^1 = CH_3, R^2 = C_2H_5$

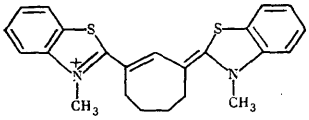

(XXVI)
$R = CH_3$

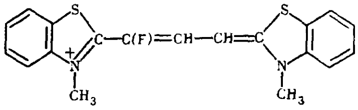
An attempt has been made to separate the steric and electronic effects of the substituents in the α- and αα′-positions in the polymethine chain on the basis of the absorption spectra of the thiacarbocyanines (XXVII).[85-88]


(XXVII)

R^1=H, CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_6H_5, OCH_3, Cl, $NHCOC_6H_5$, $N(CH_3)C_6H_5$, $COOC_2H_5$ CHO, $C_5H_5\overset{+}{N}$, SC_2H_5, SC_6H_5; R^2=H, CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_2H_5, OCH_3, SC_6H_5, Cl, $NHCOC_6H_5$, $N(CH_3)C_6H_5$.

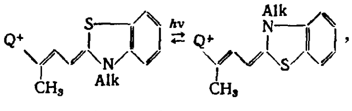
The introduction of a substituent of any electronic type as a rule induces a hypsochromic shift of the absorption maximum of the thiacarbocyanine (XXVII). The influence of a similar second substituent in the α′-position is not the same as that of the first and not only quantitatively but also qualitatively. It has been suggested[85,86] that the influence of a single substituent is associated with the breakdown of the electronic symmetry of the chromophore, while the spectroscopic changes in disubstituted dyes are determined by the competition between the electronic nature of the substituents and the steric hindrance to the planar disposition of the cation. Such hindrance commences on monosubstitution and intensifies on disubstitution, which is indicated by the corresponding decrease of the absorption intensity. The *cis*–*trans* isomerisation, which is most likely to involve peripheral bonds of the polymethine chain, probably contributes to the spectroscopic shifts. This is indicated[87] by the almost identical absorption of solutions of αα′-diethylcarbocyanine (XXVII) and the dye (XXVIII) with a seven-membered ring in the chromophore.


(XXVIII)


(XXIX)

A mixture of the *cis*- and *trans*-isomers of α-fluorothiacarbocyanine (XXIX) was detected from the absorption spectra at a low temperature.[88]

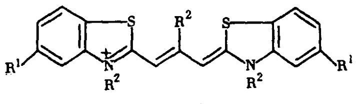
The photoisomerisation of α-substituted carbocyanines proceeds with a high quantum yield, close to that for the unsubstituted compounds. It has been suggested that the photoisomers of the compounds compared have the same nature, i.e. are *EEZ*-isomers and that the isomerisation involves the unsubstituted 2- and 8-positions:[4,89,90]

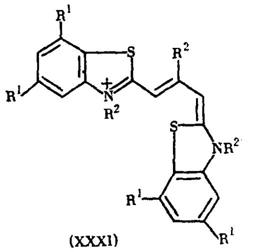


where Q is a heterocyclic nucleus.

The introduction of a bulky substituent in the β-position in the polymethine chain also intensifies the steric interaction of the fragments of the carbocyanine cation. There has been a considerable growth of interest in dyes of this kind, because β-ethylthiacarbocyanine proved to be an effective sensitiser of silver halides.[1-3]

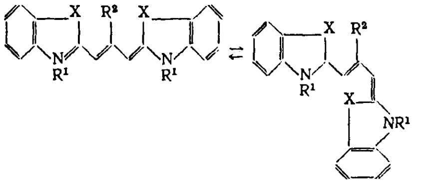
According to X-ray diffraction data, the thiacarbocyanine cation (XXX) has a distorted *EEEE*-structure. Compared with the unsubstituted dye (XXXI), the distance between the sulphur atoms is increased owing to the repulsion of the latter from the ethyl group separating them.[91] In contrast to this, the thiacarbocyanine (XXXI) exists in the solid phase in the non-planar mono-*cis*-(*EEZE*)-form.[3,92]


(XXX)
$R^1 = Cl, R^2 = C_2H_5$


(XXXI)
$R^1 = CH_3, R^2 = C_2H_5$

The β-phenylthiacarbocyanine cations exhibit in the crystals the fully *trans*-(*EEEE*) conformation.[93] The phenyl group is then rotated almost at right angles to the long axis of the cation and does not have an appreciable effect on the colour of the dye.[61]

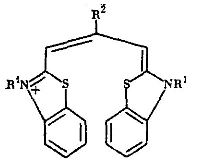
The absorption bands of solutions of β-substituted carbocyanines (XXXII) are split at low temperatures into two bands in close proximity.[78,94-97] The intensity of each band increases on excitation of the neighbouring band by irradiation at the wavelength of its absorption maximum. The cessation of irradiation entails the return of the system to the initial equilibrium state. The experimental data have been interpreted within the framework of the *cis*–*trans* isomerism of the test compound: steric interaction of the β-substituent with the terminal nuclei increases the energy of the ground state of the *EEEE*-form (XXXIIa) and makes it comparable to the energy of the *EEZE*-conformation (XXXIIb):


(XXXIIa) (XXXIIb)

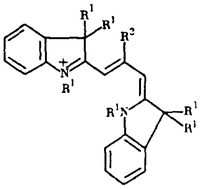
X=O, S, Se; R^1=CH_3, C_2H_5; R^2=CH_3, C_2H_5, C_6H_5, OCH_3, SCH_3

The long- and short-wavelength bands are due to the first and second isomeric forms respectively. The equilibrium position depends greatly on the solvent: the longest *trans*-isomers predominate in weakly polar media, while in strongly polar media they are present only as an admixture to the *cis*-isomer. The luminescence spectra of the carbocyanines (XXXII, R^2 = Alk, OCH_3, or SCH_3) have been investigated over a wide temperature range.[79,95-97] It has been found that the *EEZE*-isomers fluoresce only at a low temperature and that the fluorescence intensity is appreciably lower than for the *EEEE*-isomers.

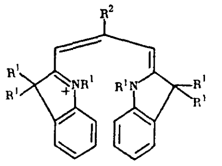
Analysis of the form and number of signals in the ^1H NMR spectra of β-substituted carbocyanines and also the observation in certain cases of the nuclear Overhauser effect make it possible to determine unambiguously the geometrical structure of the conformers and to estimate quantitatively the position of the conformational equilibrium.[75,98] It has been established that an increase of the effective bulk of the substituent in the β-position promotes an increase of the content of the *cis*-isomer. Thus the concentration of the *EEZE*-isomer of the thiacarbocyanine (XXXII) increases in the sequence $H \ll C_6H_5 < CH_3 < C_2H_5$ as R^2 is altered. As a result of the introduction of the t-butyl group, the thiacarbocyanine cation exists both in solution and in the solid phase exclusively in the form of the non-planar di-*cis*-(*EZZE*)-conformer (XXXIII).



(XXXIII)
$R^1 = C_2H_5$, $R^2 = t\text{-}C_4H_9$



(XXXIV)
$R^1 = CH_3$, $R^2 = CH_3, C_2H_5, C_6H_5$



(XXXV)
$R^1 = CH_3$, $R^2 = t\text{-}C_4H_9$

The concentration of the mono-*cis*-(*EEZE*)-isomer increases with increase of the bulk of the heteroatom X in the carbocyanines (XXXII). Finally, only the tri-*cis*-(*ZEZZ*)-form obtains in β-substituted indocarbocyanines (XXXIV), while in solution it exists in a dynamic equilibrium with the identical *ZZEZ*-form. The cation (XXXIV, $R^2 = CH_3$) has the same conformation in the crystal, the angle between the indolenine nuclei reaching 78°. The symmetrical fully *cis*-(*ZZZZ*)-conformation is fixed in the cations of the carbocyanines (XXXV). According to X-ray diffraction data, the system does not have a planar structure: the average torsional angle between the fragments of the polymethine chain is 19° and the angle between the indolenine nuclei is 41°.[98] The activation energy for the isomerisation processes is in the range 35–62 kJ mol^{-1}.[75,98]

The absorption bands of carbocyanines undergo appreciable changes on β-substitution,[2,61,98] but, among the multiplicity of steric and electronic factors, it is difficult to identify the intrinsic contribution of a particular conformation to the absorption.

The photoisomerisation of β-substituted carbocyanines has been investigated fairly widely.[4,64,80,96,99] The rate of this process for the thiacarbocyanine (XXXII, $R^1 = C_2H_5$, $R^2 = CH_3$) at −125 °C depends greatly on the nature of the halide in the solvent and increases in the sequence $C_2H_5Cl < C_2H_5Br$ C_2H_5I. This factor has been attributed[96] to the triplet mechanism of the isomerisation, whose probability increases in parallel with the increase of the spin–orbital coupling constant induced by the presence of neighbouring atoms with a higher atomic number. This factor has also been used[96] to account for the rapid isomerisation of β-methylselenacarbocyanine compared with β-methylthia- and even more so β-methyloxacarbocyanines.

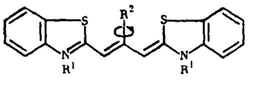
On the other hand, experiments on the triplet–triplet energy transfer have led to the hypothesis[64,99] that a singlet excited state is involved exclusively in the photoisomerisation at room temperature and that its degradation takes place in accordance with the scheme

$$
{}^0S_{trans(cis)} \xrightarrow{h\nu} {}^*S_{trans(cis)} - \left| \begin{array}{l} \rightarrow {}^0S_{trans(cis)} \text{ (fluorescence),} \\ \rightarrow {}^1T_{trans(cis)} \text{ (intersystem crossing),} \\ \rightarrow {}^0S_{trans(cis)} \text{ (internal transition),} \\ \rightarrow {}^0S_{cis(trans)} \text{ (isomerisation);} \end{array} \right.
$$

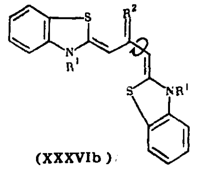
$$
{}^0S_{cis(trans)} \rightarrow {}^0S_{trans(cis)} \text{ (dark reaction).}
$$

According to this scheme, three radiationless processes compete: isomerisation, internal transition, and intersystem crossing. In carbocyanines, with the exception of β-iodothiacarbocyanine, the last process takes place with an extremely low quantum yield. The main factor determining which of the two first processes predominate is steric hindrance to the planar structure of the photoisomer. In contrast to unsubstituted and α-substituted carbocyanines, in the molecules of β-substituted dyes the dominant process leading to the degradation of the excited state is internal transition. The unusually high quantum yield in the photoisomerisation of β-fluorothiacarbocyanine can be explained by the small size of the fluorine atom, which permits isomerisation with respect to the C(2)–C(8) bond.

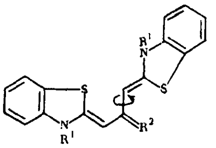
An unusual kind of isomerism, called "allopolar", has been described.[2,100] An obligatory condition for systems having the general formula (XXXVI) and undergoing this type of isomerism is the presence in the polymethine chain of bulky substituents R^2, containing π electrons which can interact under certain conditions with the main π-electron system of the molecule.



(XXXVIa)

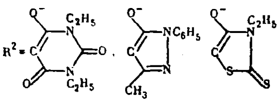


(XXXVIb)



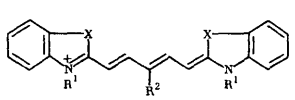
(XXXVIc)

$R^1 = C_2H_5$; $R^2 =$

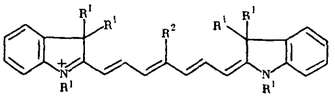


In the betaine (holopolar) form (XXXVIa), the steric interaction between the substituent R^2 and the heterocyclic nuclei makes the plane of the substituent perpendicular to the long axis of the carbocyanine part of the molecule and the influence of the substituent on the electronic absorption spectrum is purely inductive in character. The second isomeric merocyanine form (XXXVIa) is characterised by the fact that the π electrons of the substituent R^2 form a single chromophoric system with one half of the molecule, the second half being perpendicular to the new chromophore. An alternative form is the *trans*-(*EE*)-isomer (XXXVIc). The forms presented above absorb in different parts of the spectrum and this type of isomerism can therefore be observed at room temperature. The ratio of the isomers is sensitive to changes in the dielectric properties of the medium. It has been shown that polar and proton-donating solvents increase the content of the charged form (XXXVIa), while non-polar and aprotic solvents tend to increase the content of the merocyanine forms (XXXVIb, c).

There is little information about the steric structure of the dicarbocyanines (XIII, $m = 2$) and higher vinylene homologues. It is known that the cations of the thiadicarbocyanine (XXXVII, $R^1 = C_2H_5$, $R^2 = H$), indodicarbocyanine (XXXVII, $R^1 = CH_3$, R^2 = cyclopropyl), and indotricarbocyanine [XXXVIII, $R^2 = CH_2CH(OCH_3)_2$] exist in the solid phase in the fully *trans*-conformation and are almost planar.[100–102]



(XXXVII)
X = S, $C(CH_3)_2$; $R^1 = CH_3, C_2H_5$; $R^2 = H, OCH_3, C_3H_5, C_4H_7, C_6H_{11}, CH_3, C_6H_5$, F, Cl, Br, I, $C_6H_5N_2$, CHO, CN, NO_2

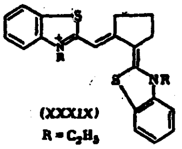


(XXXVIII)
$R^1 = CH_3$; $R^2 = H, CH_2CH(OCH_3)_2$

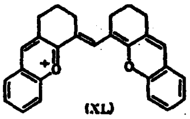
^1H and ^{13}C NMR studies of various γ-substituted dicarbocyanines (XXXVII) and also the indotricarbocyanine (XXXVIII, $R^2 = H$) have shown that these compounds exist in solution exclusively in the fully *trans*-conformation, favouring, other conditions being equal, the maximum overlap of the orbitals and the delocalisation of π electrons.[103-108] These data conflict with the earlier report[109] of the separation of three isomers by chromatographing thiatricarbocyanine on calcium carbonate at room temperature.

Only the photoexcited forms of the stereoisomers of the dicarbocyanines, which as a rule absorb at longer wavelengths than the corresponding forms in the ground state, can be detected.[4,80,110,111] The number of possible steric forms of dicarbocyanines is much greater than for dyes with a shorter polymethine chain. Thus the indodicarbocyanines (XXXVII, R^2 = H or F) give rise to several forms—short-lived (lifetime $\tau = 10^{-6}$ s) and long-lived ($\tau = 10^{-2}$ s).[111] The unstable photoisomers have the sterically highly hindered and therefore non-planar di-*cis*-structure. The angle of rotation of the chromophore fragment is closer to 180° on formation of the long-lived photoisomers but the latter are not fully planar either.

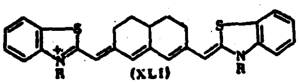
This factor is precisely the reason why the photoisomers fluoresce much less effectively than the corresponding forms in the ground state. This leads to losses in the excitation band owing to the overlap of the fluorescence spectrum of the generating form in the ground state and the absorption spectrum of the photoisomer. Another cause of the impairment of the generating properties of polymethine dyes is the "depletion" of the first excited singlet state owing to losses in the isomerisation proper.[4,5,112,113] These causes may be eliminated by the partial [the cations (XXXIX)–(XLI)] or complete [the cations (XLII) and (XLIII)] fixation of the chromophore in a particular conformation.[114-119]



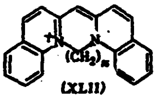
(XXXIX) R = C_2H_5



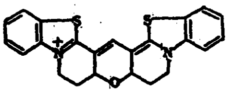
(XL)



(XLI) R = C_2H_5

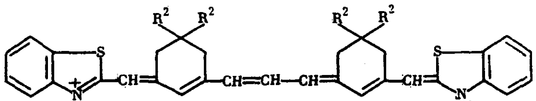


(XLII) n = 1, 2



(XLIII)

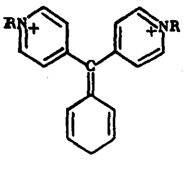
Taking into account the entropy factor, it might have been supposed that an increase in the length of the polymethine chain would reduce the probability of the existence of the di-cations in the fully *trans*-conformation, as happens, for example, in the molecules of saturated linear hydrocarbons.[8] Thus the short-wavelength absorption of the cation (XLIV) has been explained[120] by the existence of the *cis*-isomer. On the other hand, recent studies[121,122] have shown that polycarbocyanines exist in solution in the form of solvates absorbing in different parts of the spectrum.



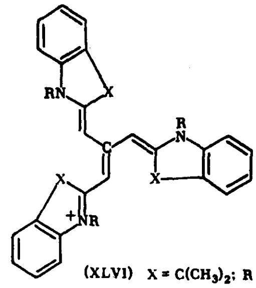
(XLIV)

$R^1 = C_2H_5$; $R^2 = CH_3$

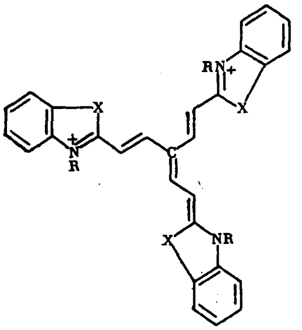
The so-called trinuclear dyes (XLV)–(XLVIII) constitute a special group. They differ by the fact that the *meso*-substituent is yet another heterocyclic nucleus linked directly to the polymethine chain [compound (XLV)] or via the methine [compound (XLVI)], vinylene [compound (XLVII)], or propenylene [compound (XLVIII)] groups. It has been shown from NMR data that the cations or di-cations of these compounds have a propeller-like structure and possess a threefold symmetry axis passing through the central carbon atom.[60,102,103,123] This configuration of the cation (XLVIII) is realised in the crystal.[102]



(XLV) R = CH_3

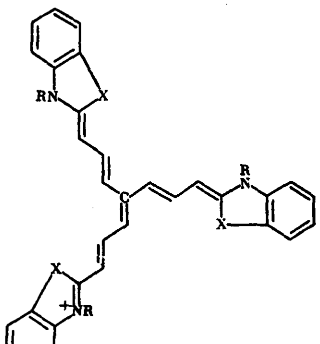


(XLVI) X = $C(CH_3)_2$; R = CH_3, C_2H_5



(XLVII)

X = $C(CH_3)_2$, S, CH=CH; R = CH_3, C_2H_5



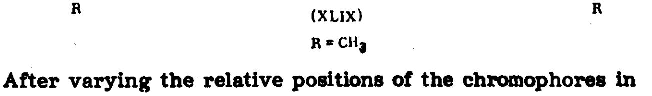
(XLVIII)

X = $C(CH_3)_2$; R = CH_3, C_2H_5

IV. ABSORPTION SPECTROSCOPIC STUDY OF THE CONFORMATIONAL FEATURES OF POLYMETHINE DYES WITH TWO CHROMOPHORES

As mentioned above, electronic spectra proved to be relatively unsuitable for the investigation of the conformations of polymethine dyes owing to the multiplicity of factors masking the contribution of the particular conformation to the absorption. On the other hand, the phenomenon of the interaction of chromophores, discovered by Kiprianov and Mushkalo,[124] showed that the scope of electronic spectroscopy can be greatly increased. A fundamentally new approach to the problem of the study of the conformations of polymethines is based on the characteristic features of the interaction of chromophores bound in a single molecule, in particular on the postulate that the ratio of the intensities of two absorption bands is determined ay the angle between the directions of the chromophores (ADC) in the cation.[15]

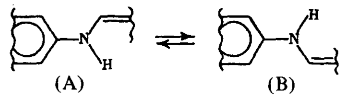
The spectroscopic properties of the readily available hemicyanines (XLIX, n = 0 or 1), which can be regarded as streptocyanines with rigidly fixed terminal arene nuclei, were investigated in the first place:

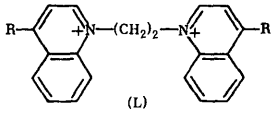


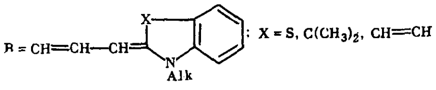
(XLIX)

R = CH_3

After varying the relative positions of the chromophores in structural isomers by introducing an aryl or heteroaryl connecting nucleus, by introducing various substituents into the latter, and by altering the solvation properties of solvents, the authors[124-132] concluded, from the ratio of the intensity of the two absorption bands, that the conformational equilibrium between the two planar forms (A) and (B) of the hemicyanine fragment is very mobile and depends on all the factors enumerated.


(A) (B)

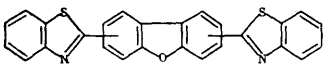

(L)

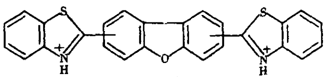


The conformations of the biscarbocyanine (L), in which the heterocyclic nuclei are linked by a polymethine bridge, have been discussed.[132] As in the spectra of bishemicyanines, the ratio of the intensities of the longest-wavelength absorption band in the spectrum of this dye depends on the ADC in each conformer, formed as a result of the hindered rotation about the single bonds in the ethylene connector, and also on the concentration of a particular conformer. It has been shown that an increase of solvent polarity is accompanied by an increase of the intensity of the short- at the expense of the long-wavelength band, i.e. by a shift of the conformational equilibrium towards the formation of skewed (*gauche*) conformers.

The shift towards the formation of the more "compact" conformer (L) takes place also when a high pressure is applied to the solution of the dye.[133]

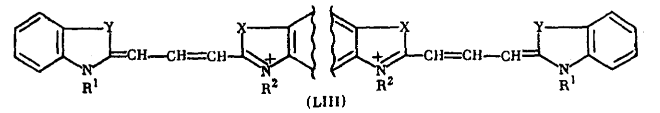
The absorption spectra of the highly coloured dibenzothiazolyldibenzofurans (LI) and their simple salts (LII) have been examined within the framework of the theory of the interaction of chromophores. The positions and intensities of the bands in the spectra of all the possible planar conformers, formed on rotation of the benzothiazole groups about the bonds with the dibenzofuran nucleus, have been evaluated by quantum-chemical calculation.[134]


(LI)


(LII)

Unfortunately the broad overlapping absorption bands hinder the interpretation of the spectra of the majority of the compounds mentioned.

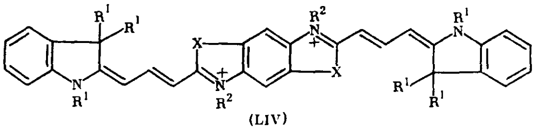
The biscarbocyanines (LIII), in which the central nucleus has a rigid structure and which give rise to narrow well resolved absorption bands, proved to be a much more successful model for the study of the characteristic features of the interaction of chromophores:[6,15,135,136]

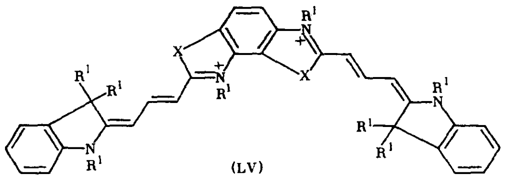

(LIII)

X, Y = O, S, $C(CH_3)_2$; R^1, R^2 = CH_3, C_2H_5

These systems proved to be extremely suitable also for the solution of conformational problems.[137-140]

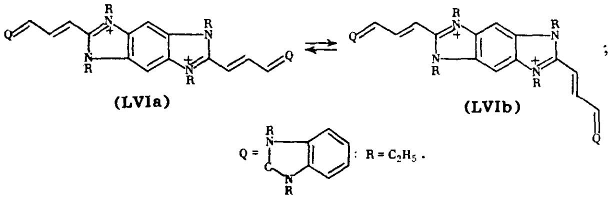
The fact that the fully *trans*-conformation is the only one for both polymethine chains of the biscyanines (LIII) has been confirmed by the complete similarity of the forms of the absorption curves within each of two families of dyes (LIV) and (LV) in which the ADC should be identical for structural reasons regardless of the bond lengths and valence angles.[137]


(LIV)

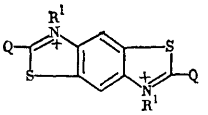

(LV)

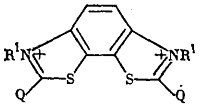
X = O, S, $C(CH_3)_2$; $R^1 = CH_3$; $R^2 = CH_3, C_2H_5$

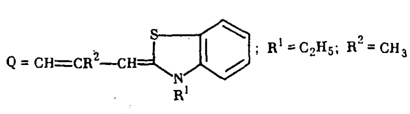
The identity of the forms of the absorption curves is consistent with the presence of one and only one conformation of the chromophores. The presence in solution of several conformers, each of which has its own ADC, should ultimately affect the ratio of the band intensities. For example, by virtue of its high symmetry, the biscyanine (LVI) can exist in two almost equally probable forms (LVIa) and (LVIb), in one of which the ADC is 180° and in the other 120°. An appreciable short-wavelength band is observed precisely because of the conformational inhomogeneity in the absorption spectrum of the biscyanine (LVI).[137]


(LVIa) (LVIb)

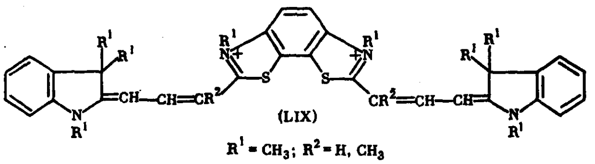
The synthesis and spectroscopic study of the biscarbocyanines (LVII) and (LVIII) with bulky substituents in the β-position in the polymethine chain made it possible to observe the conformational equilibrium between the fully *trans*- and *cis*-forms at room temperature without resorting to special measuring techniques.[137] In the former case the conformational homogeneity is manifested by a distinct short-wavelength band. The presence of this band rules out the possibility that steric hindrance may be eliminated exclusively as a result of the alteration of the valence angles between the atoms of the polymethine chain, since in this case the ADC of 180° would have been retained.


(LVII)


(LVIII)



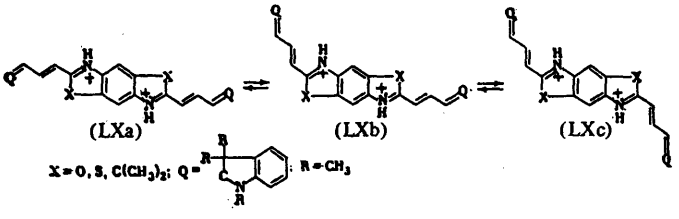
The introduction of a methyl group in the α-position in one and then in the other polymethine chain [in the dyes (LIX)] make it possible to follow the appearance of the corresponding *cis*-isomers from the relative increase of the intensity of the long-wavelength band.[137]



(LIX)

$R^1 = CH_3$; $R^2 = H, CH_3$

The appearance of *cis*-conformations in the two previous cases (α- and β-substitution) is associated with the increase in the steric interaction in the di-cations. The example of NH-biscyanines shows, on the contrary, that conformational inhomogeneity can arise on replacement of the bulky methyl group at the nitrogen atoms of the terminal heterocycles by a hydrogen atom.[138-140] Thus there is no short-wavelength band in the spectrum of *N*-methylated dyes (LIV). This is consistent with the fully *trans*-disposition of both polymethine chains, forming an angle of 180°. However, for the NH-biscyanines (LX) this *trans,trans*-conformer (LXa) is only one of the three possible conformers. Although another conformer (LXc), corresponding to the *cis*-configuration of each polymethine chain, also does not contribute to the short-wavelength absorption, the chromophores of the non-centrosymmetric *cis,trans*-conformer (LXb) form an ADC less than 180°; the short-wavelength band of this particular conformer is in fact partly allowed. If instead of conformational changes the fully *trans*-polymethine chains were fully displaced into the space previously occupied by methyl groups, the ADC would have remained 180° and the prohibition of the short-wavelength band would have remained in force:

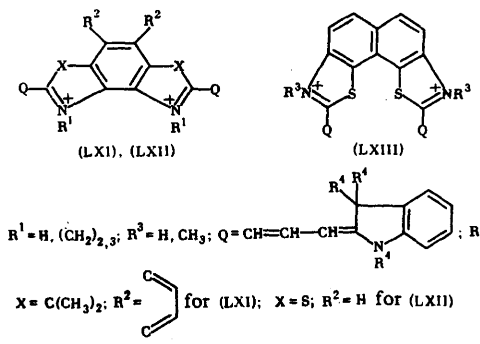


(LXa) (LXb) (LXc)

X = O, S, $C(CH_3)_2$; Q = ; R = CH_3

The conformational changes can be followed most clearly from the absorption spectra of biscyanines with angular central nuclei.

The considerable predominance of the long- over the short-wavelength band in the absorption spectra of the biscyanines [LXI, $R^1 = (CH_2)_{2,3}$] is determined by the obtuse ADC, to which correspond the *trans*-conformations of both polymethine chains. The replacement of the alkylene bridge by hydrogen atoms [in the dye (LXI, R^1 = H)] leads to the inversion of the intensities of the bands with retention of their positions. This is caused by the presence in the equilibrium mixture of the conformer (LXI) whose polymethine chains are in the *cis*-conformations and form an acute angle.



(LXI), (LXII) (LXIII)

$R^1 = H, (CH_2)_{2,3}$; $R^3 = H, CH_3$; Q = CH=CH—CH= ; $R^4 = CH_3$;

X = $C(CH_3)_2$; R^2 = for (LXI); X = S; R^2 = H for (LXII)

The bisthiacyanines (LXII) are structural analogues of the dyes (LXI) but the redistribution of band intensities on passing to NH-biscyanine is not so great. This is associated with the smaller fraction of the *cis,cis*-conformer in the thiazole dye compared with the pyrrolenine dye.[140]

On the other hand, appreciable spectroscopic changes occur after the gradual replacement of the *N*-methyl groups by hydrogen atoms in bisthiacarbocyanines (LXIII). Calculation of the conformational equilibrium[140] has shown that the fraction of the *cis*-conformers of the dyes (LXIII) is greater than for the remaining NH-cyanines derived from benzobisthiazoles. This is caused by the mutual repulsion of chromophores bearing like charges, which is a maximum for conformers with chromophores in structural proximity and a minimum for conformers such as (LXa) and (LXc), i.e. with chromophores remote from one another. In the latter case the conformational equilibrium depends on the steric factor, which is determined by the relative dimensions of the groups NH and X. The Coulombic repulsion of the chromophores is also the cause of the distinct dependence of the conformational equilibrium on the dielectric properties of the medium.[138-140]

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Thus it is now possible to identify the main factors on which the steric structures of polymethine dyes depend, including their tendency to exist in the form of different conformers. These are the nature of the terminal heterocyclic nucleus and the substituent at its nitogen atom, the length of the polymethine chain, the effective bulk of the substituent and the site where it is introduced, the properties of the medium, and also the molecular interaction (the possibility of aggregation).

However, despite the evident advances which have been achieved as the spectroscopic technique has been improved and new systems have been synthesised, the identification of conformers remains a fairly complex task to this day. In view of the low activation barrier of the isomerisation process (33–63 kJ mol^{-1}), it is not possible to separate the conformers and to isolate them in a pure state. X-Ray diffraction analysis requires special conditions as regards the preparation of crystalline specimens, which frequently cannot be fulfilled. The geometrical structure of the di-cations in the crystal can differ appreciably from their state in solution. The electronic spectra, which are the most important characteristics of the dyes, are relatively unsuitable in this instance. The amount of information derivable from them increases appreciably in the case of biscyanines, but this involves considerable difficulties in the synthesis of suitable objects. A more effective method for the determination of the steric structures of methine dyes is NMR.

In the future one may probably expect that studies devoted to the conformational analysis of cyanines with non-traditional heterocyclic nuclei and also containing a wider range of substituents will be carried out. The problems postulated will be solved by improving and employing on a wider scale the physicochemical and special synthetic methods.

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Hexafluoroisopropylidene-containing Polyheteroarylenes

V.V.Korshak, I.L.Knunyants, A.L.Rusanov, and B.R.Livshits

The methods of synthesis of various condensation monomers containing the hexafluoroisopropylidene groups and the polyheteroarylenes based on them are examined. The influence of the hexafluoroisopropylidene groups incorporated in the main chains of the macromolecules is analysed and it is shown that polyheteroarylenes containing these are characterised by an improved solubility and fire resistance and that the articles based on them have a higher elasticity.
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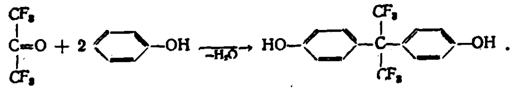
I. INTRODUCTION

Halogen and in particular fluorine-containing condensation polymers have attracted much attention by investigators in the course of the last 25 years. A series of monographs and careful reviews,$^{1-5}$ indicating the enormous variety of the halogen-containing polymers synthesised and their properties, have been devoted to the principal advances in this field. Among the numerous fluorine-containing polymers, aromatic polycondensation systems are of special interest$^{1-3}$ and among them those where the fluorine atoms are located in the side chains and not in the benzene ring.^{3} Typical representatives of such polymers are polycondensates containing hexafluoroisopropylidene groups. A systematic analysis of the advances in this field is not available in the literature. For this reason, the selected subject of this review is an examination of the advances in the synthesis and investigation of condensation monomers and polyheteroarylenes containing hexafluoroisopropylidene groups.

II. CONDENSATION MONOMERS CONTAINING HEXAFLUOROISOPROPYLIDENE GROUPS

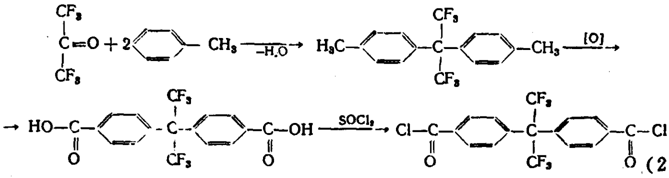
The synthesis of condensation monomers containing hexafluoroisopropylidene groups is based on the reactions of hexafluoroacetone with various aromatic compounds containing mobile hydrogen atoms$^{6-11}$ and the subsequent reaction of the simplest condensation products.$^{7-18}$

Thus Knunyants and co-workers^{16} achieved the condensation of hexafluoroacetone with phenol in the presence of anhydrous HF, which resulted in the formation of 2,2-di(p-hydroxyphenyl)hexafluoropropane produced at the present time in considerable amounts and known under the name "bisphenol AF":^{11}



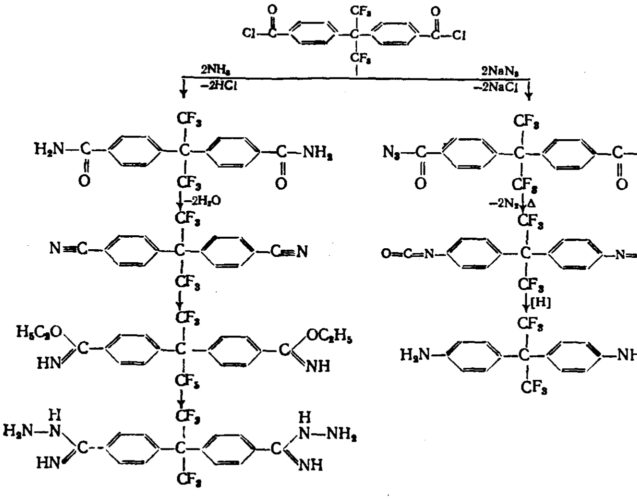
(1)

The development of this approach to the synthesis of bifunctional derivatives of 2,2-diarylhexafluoropropane led to the formation of a whole series of compounds with hexafluoroisopropylidene groups,$^{7-10}$ which are of independent interest as monomers for polycondensation or serving as intermediates in the synthesis of condensation monomers with a complex structure. In particular, a dicarboxylic acid and acid dichloride derived from 2,2-diarylhexafluoropropane have been obtained by condensing hexafluoroacetone with toluene and subsequent reactions of 2,2-di(4-tolyl)hexafluoropropane:$^{7-10}$



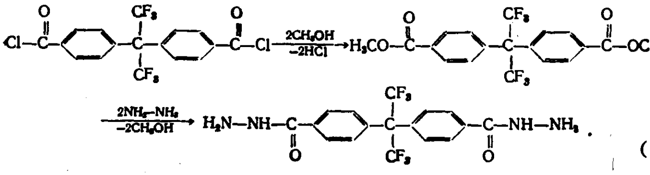
(2)

Subsequent reactions of the dichloride of 2,2-di(p-carboxyphenyl)hexafluoropropane led to the formation of the corresponding diamide, diazide, diisocyanate, and diamine$^{7-9}$ as well as the dinitrile, the diethyl bis(iminoester), and the bisamidrazone of 2,2-di(p-carboxyphenyl)hexafluoropropane:



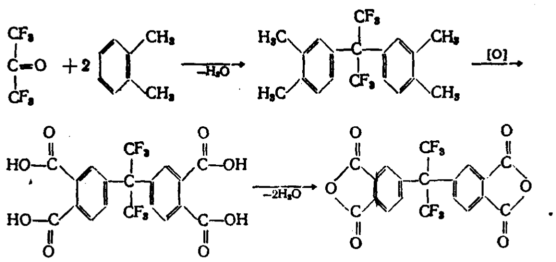
(3)

Subsequently the diphenyl ester, the dimethyl ester, and the dihydrazide of 2,2-di(p-carboxyphenyl)hexafluoropropane were synthesised:^{8}



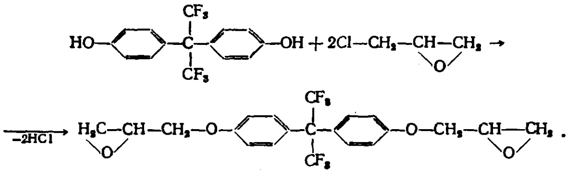
(4)

2,2-Di(3,4-dimethylphenyl)hexafluoropropane, whose oxidation yielded 2,2-di(3,4-dicarboxyphenyl)hexafluoropropane, dehydrated subsequently to the corresponding dianhydride, was obtained by the reaction of hexafluoroacetone with *o*-xylene:[9]



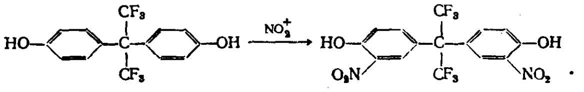
(5)

Evidently the final products and the series of intermediates indicated in Schemes (1)–(5) refer to the majority of the classes of monomers used in polycondensation reactions.[12] On the other hand, many of them have been used in various reactions leading to new monomers. 2,2-Di(4-hydroxyphenyl)hexafluoropropane is used particularly vigorously for this purpose. Thus the di(4-glycidyl) ether of 2,2-di(4-hydrophenyl)hexafluoropropane has been synthesised by its interaction with epichlorohydrin:[13,19]



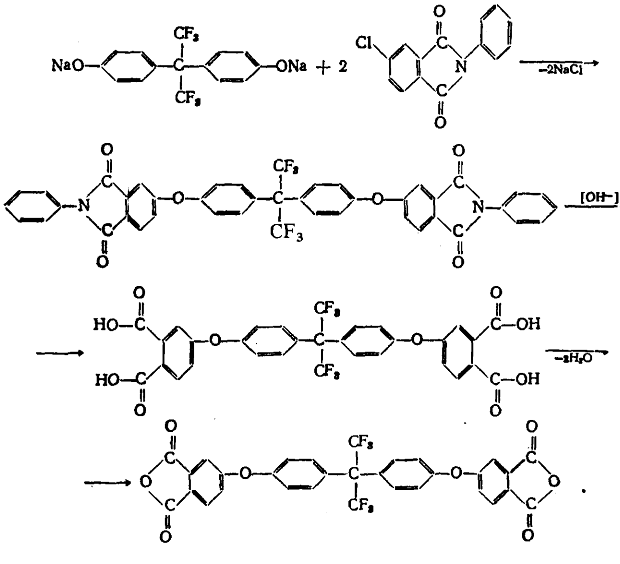
(6)

The nitration of this bisphenol yielded 2,2-di(4-hydroxy-3-nitrophenyl)hexafluoropropane:[14]



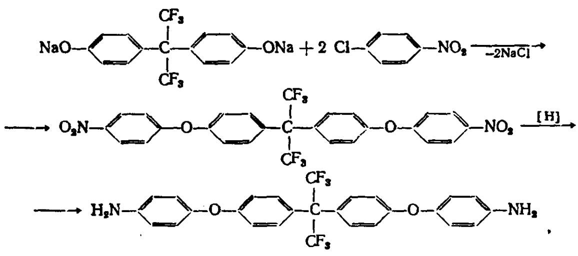
(7)

The reaction of its disodium salt with 4-chloro-*N*-phenylphthalimide and subsequent reactions of the latter afforded the dianhydride of 2,2-di[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane:[15,16]



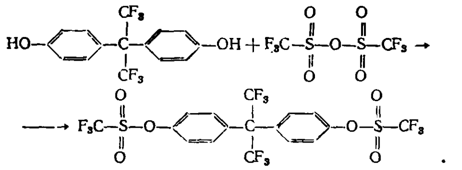
(8)

The interaction of the same diphenoxide with twice the molar amount of *p*-chloronitrobenzene made it possible to obtain 2,2-di[4-(4-nitrophenoxy)phenyl]hexafluoropropane, which was subsequently reduced to 2,2-di[4-(4-aminophenoxy)phenyl]hexafluoropropane:[18]



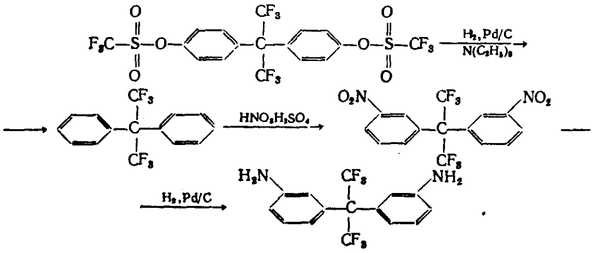
(9)

A considerable amount of hexafluoroisopropylidene-containing monomers have been synthesised[11] from 2,2-di(4-trifluoromethanesulphonyloxyphenyl)hexafluoropropane, obtained by treating bisphenol AF with trifluoromethanesulphonic (triflic) anhydride:[20,21]



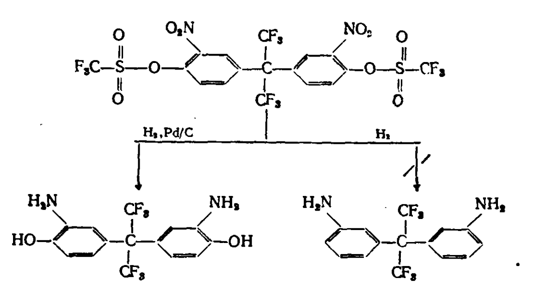
(10)

The ditriflate obtained in this way was reduced catalytically over palladium on charcoal in the presence of triethylamine. This resulted in the formation of 2,2-diphenylhexafluoropropane, whose nitration and subsequent reduction afforded 2,2-di(3-aminophenyl)hexafluoropropane:[11]



(11)

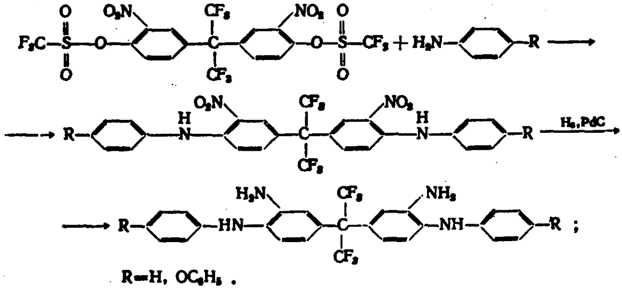
The nitration of the ditriflate gave rise to 2,2-di(3-nitro-4-trifluoromethane-sulphonyloxyphenyl)hexafluoropropane, whose hydration led to the formation of 2,2-di(3-amino-4-hydroxyphenyl)hexafluoropropane instead of the expected 2,2-di(3-aminophenyl)hexafluoropropane:[11]



(12)

We may note that the former product can apparently be obtained also by a simple procedure via the nitration of bisphenol AF[14] and the reduction of the resulting 2,2-di(4-hydroxy-3-nitrophenyl)hexafluoropropane.

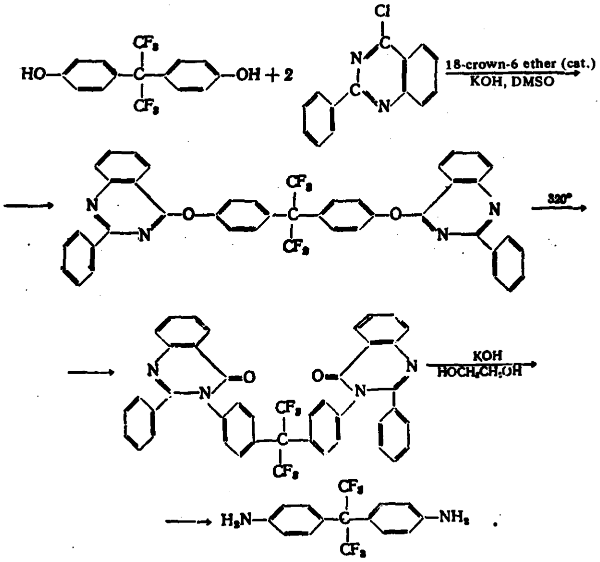
The replacement of the triflate group in 2,2-di(3-nitro-4-trifluoromethane-sulphonyloxyphenyl)hexafluoropropane by aromatic amines with subsequent reduction of the reaction product led to the formation of various 2,2-di(3-amino-4-arylamino)hexafluoropropanes:[11]



R=H, OC_6H_5.

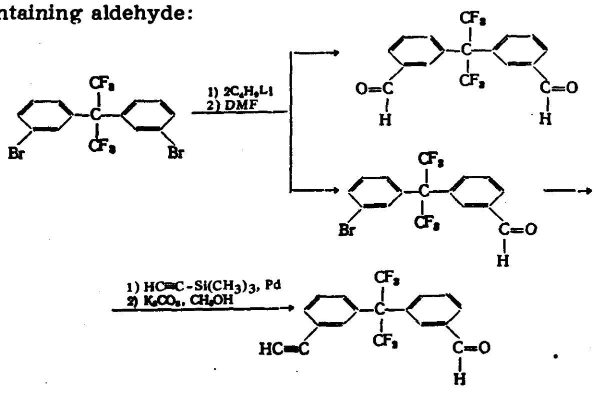
(13)

Finally bisphenol AF has been converted[11] into 2,2-di(4-aminophenyl)hexafluoropropane. A method, which is general for the conversion of phenols and bisphenols into amines and diamines, was used for this purpose:



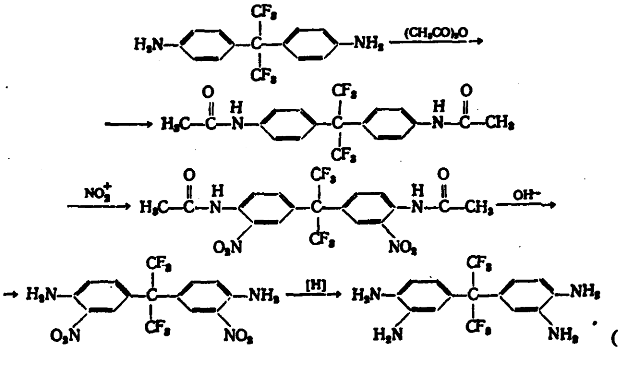
(14)

New monomers have been obtained via a series of reactions also from the isomeric hexafluoroisopropylidene-containing aromatic diamines. Thus 2,2-di(3-aminophenyl)hexafluoropropane was converted via the Sandmeyer reaction into 2,2-di(3-bromophenyl)hexafluoropropane,[11] which was in its turn converted by treatment with organolithium compounds into 2,2-di(3-formylphenyl)- and 2-(3-bromophenyl)2-(3-formylphenyl)hexafluoropropanes and further into an ethynyl-containing aldehyde:



(15)

The corresponding bis(o-phenylenediamine) has been obtained from 2,2-di(4-aminophenyl)hexafluoropropane via stages involving the acetylation of the amino-groups, nitration, the removal of the acyl protecting group, and reduction of the resulting 2,2-di(4-amino-3-nitrophenyl)hexafluoropropane:[9]

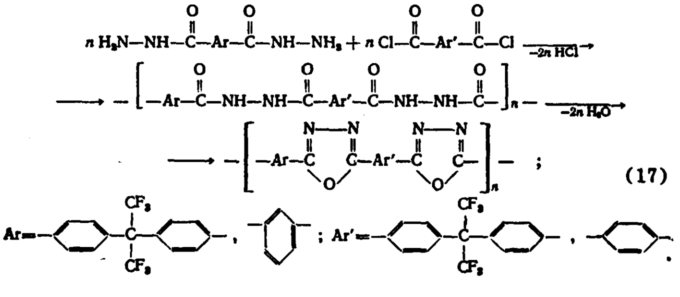


(16)

The simplest monomers containing hexafluoroisopropylidene groups were used successfully at the beginning of the 1960's for the synthesis of heterochain polymers—polyesters,[23] polycarbonates,[23,24] polyarylates,[25] polyamides,[26] polyurethanes,[8] etc. In these and later[27] studies it was already shown that the trifluoromethyl groups as side substituents at the central carbon atom significantly improve the mechanical properties of the polymers and sharply increase their solubility in any solvent, improving thereby their capacity for being worked and converted into articles. Since the capacity for being converted into articles and the deformation-strength characteristics of the latter are in fact the weak features of many polyheteroarylenes,[28] it appeared entirely natural to synthesize polyheteroarylenes containing hexafluoroisopropylidene groups in order to modify the properties of these systems in the required direction.

III. POLYHETEROARYLENES CONTAINING HEXAFLUOROISOPROPYLIDENE GROUPS IN THE MAIN CHAINS OF THE MACROMOLECULES

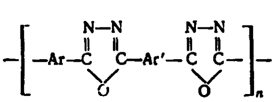
One of the first polyheteroarylenes which have attracted the attention of investigators as regards their modification by hexafluoroisopropylidene groups were poly-1,3,4-oxadiazoles.[27,29] These polymers were synthesised using a traditional approach,[30,31] via the interaction of the dihydrazide and (or) dichloride of 2,2-di(p-carboxyphenyl)hexafluoropropane with monomers of the dihydrazide and acid dichloride series with subsequent thermal cyclisation of the resulting polyhydrazides:[27,29]

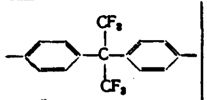
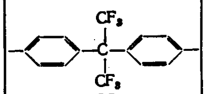
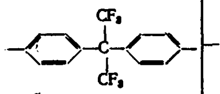
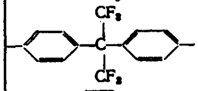
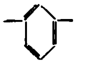


Certain characteristics of the poly-1,3,4-oxadiazoles synthesised in this way are presented in Table 1.

Analysis of the data in Table 1 indicates a significant (~50 °C) decrease of the softening temperature of the polyoxadiazoles on passing from the structure lacking hexafluoroisopropylidene groups to one containing the maximum number of the latter. On the other hand, the solubility of poly-1,3,4-oxadiazoles increases with increase of the content of fluorine atoms in the polymer. Polymers based on the dichloride of 2,2-di(p-carboxyphenyl)hexafluoropropane and its dihydrazide are the most soluble.[27] The tendency of the fluorine-containing polymers to dissolve can be accounted for, according to Livshits et al.,[27] both by the affinity of the trifluoromethyl groups for polar solvents and by the nonrigid structure of these polymers as a consequence of the presence in them of bulky groups facilitating the diffusion of the solvent.

Table 1. Certain characteristics of poly-1,3,4-oxadiazoles having the general formula[27,29]



Ar	Ar′	T^{*}_{soft}	Solubility**			
			nitro-benzene	TCE : phenol (3:1)	DMF	DMSO
		370	∓	∓	+	∓
		360	∓	+	+	∓
		330	+	+	+	+
		380	−	−	−	−

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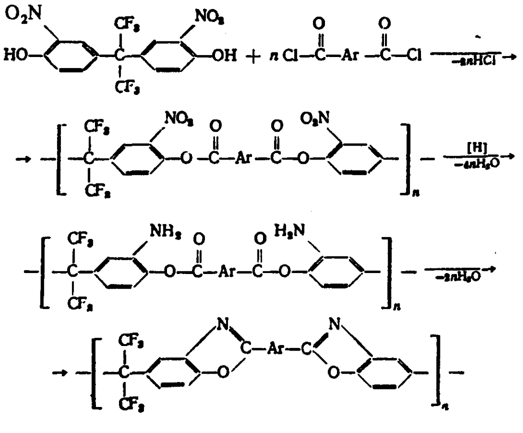
*Here and henceforth the softening temperature T_{soft} is assumed to be the value obtained from the thermomechanical curves.

**Here and henceforth the following notation has been adopted in designating solubilities: +—soluble in the cold, ±—soluble on heating, ∓—swells, —insoluble.

It is noteworthy that the data presented in Table 1 refer to polymers obtained by thermal solid-phase polycyclisation (at 275 °C for 20 h). It might have been expected that catalytic cyclisation in solution would lead to the formation of polymers with a still higher solubility. Overall, poly-1,3,4-oxadiazoles containing hexafluoroisopropylidene groups are promising polymers and, provided that the problem of the starting materials can be solved successfully, they may be of significant practical interest.

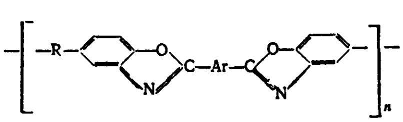
The synthesis of polybenzoxazoles containing hexafluoroisopropylidene groups has also attracted much attention by investigators. These polymers have been obtained by the reductive polyheterocyclisation reaction[14,32] in accordance with the scheme[14,32-34]

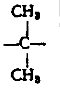
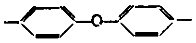
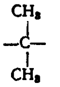
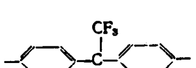
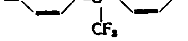
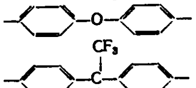
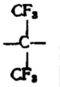
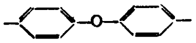
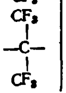
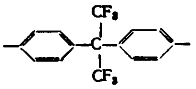


(18)

The synthesis in *N*-methyl-2-pyrrolidinone (N-MP) using reduced iron and HCl, which play simultaneously the role of a reductant and the cyclisation catalyst, led to the formation of high-molecular-weight polymers characterised by high degrees of cyclisation. Certain characteristics of the polybenzoxazoles synthesised are presented in Table 2.

Table 2. Certain characteristics of polybenzoxazoles having the general formula[14]



R	Ar	η^{*}_{int}, dl g^{-1}	T^{**}_{soft}, °C	T_{decomp}, °C	Solubility	
					TCE:phenol (3:1)	N-MP
 $-C(CH_3)_2-$		1.20	260—270	400	+	−
 $-C(CH_3)_2-$		1.32	250—260	360	+	+
$-CH_2-$		1.48	280—290	435	+	−
$-CH_2-$		1.37	280—270	410	+	−
 $-C(CF_3)_2-$		0.82	270—280	420	+	+
 $-C(CF_3)_2-$		1.08	240—250	370	+	+

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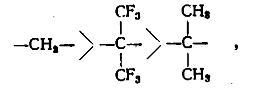
*The intrinsic viscosity (η_{int}) was determined in a 3:1 TCE—phenol mixture at 25 °C.

**Here and henceforth the decomposition temperature (T_{decomp}) was assumed to be the temperature at which 10% of the mass was lost under the conditions of dynamic TGA (in air, ΔT = 4.5 K min^{-1}).

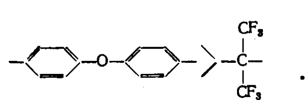
Analysis of the data in Table 2 indicates the relation between the structure and properties of the polymers, which is identical with that found for poly-1,3,4-oxadiazoles (Table 1): the replacement of the traditional aromatic "bridging" groups by hexafluoroisopropylidene fragments leads to the improvement of the solubility of the polymers and at the same time to a decrease of the softening temperatures, the combination of the two factors improving the capacity of polybenzoxazoles for being worked.

Data on the thermal stability of the polyheteroarylenes synthesised have attracted attention. Despite the rather arbitrary nature of the data obtained under the conditions of dynamic thermogravimetric analysis (DTA) thermal stability series are quite clearly manifested: in relation to the "bridging" groups R, series have the following form:



$$-CH_2- > -C(CF_3)_2- > -C(CH_3)_2- \quad (19)$$

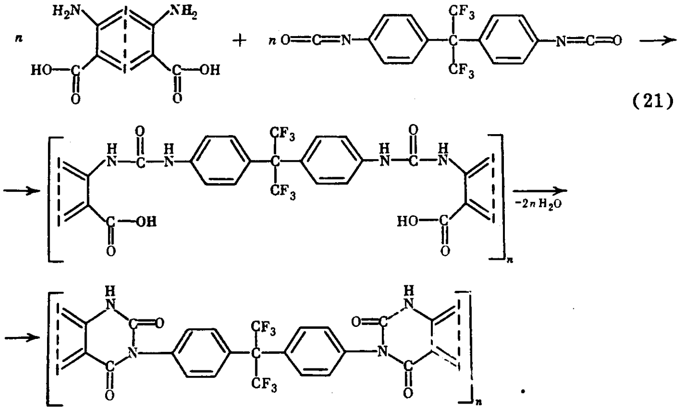
while in relation to dicarboxylic acid residues Ar it is



$$-C_6H_4-O-C_6H_4- > -C(CF_3)_2- \quad . \quad (20)$$

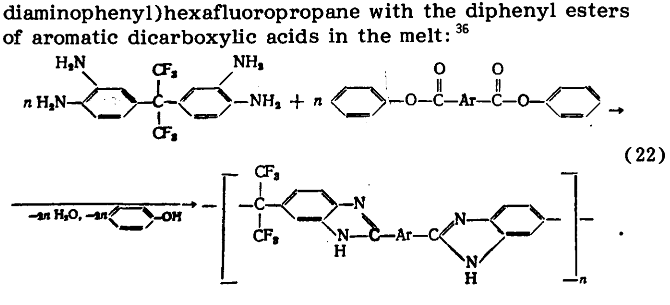
The data obtained agree both with the results of a study[23] where it was claimed that the thermal stability of the polycarbonate based on 2,2-di(4-hydroxyphenyl)hexafluoropropane is greater than that of the polycarbonate based on bisphenol A and with the results of an investigation[27] in which a reduced thermal stability of polyheteroarylenes containing hexafluoroisopropylidene groups was claimed.

The data on the synthesis of polyquinazolinediones[35] and polybenzimidazoles[36] containing hexafluoroisopropylidene groups appear to be somewhat less systematic. Polyquinazolinediones containing hexafluoroisopropylidene groups have been obtained by the reaction of bis(anthranilic acids) with 2,2-di(4-isocyanatophenyl)hexafluoropropane:[35]



(21)

Polybenzimidazoles containing hexafluoroisopropylidene groups have been obtained by the reaction of 2,2-di(3,4-diaminophenyl)hexafluoropropane with the diphenyl esters of aromatic dicarboxylic acids in the melt:[36]



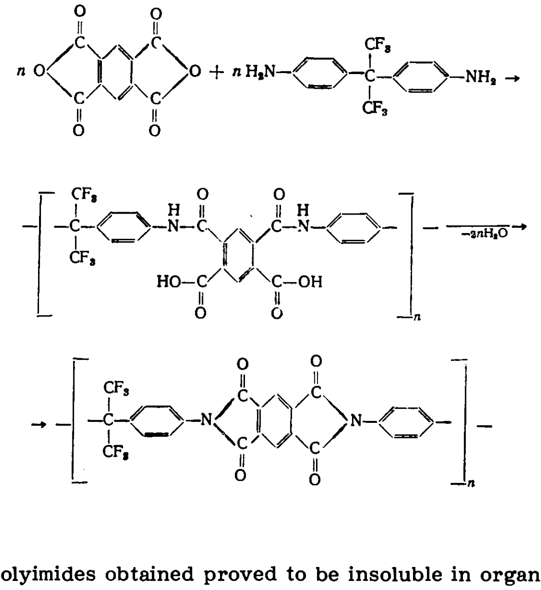
(22)

In all cases the introduction of hexafluoroisopropylidene groups led to the changes in the properties of polymers noted above and in addition to an appreciable increase of their fire resistance. The latter factor is extremely important in view of the considerable interest in fire resistant polymers.[37] Almost all investigators are unanimous in claiming a positive influence of the trifluoromethyl groups on the fire resistance of polymers, but in most cases the results obtained are qualitative rather than quantitative, which naturally hinders the analysis of the dependence of this property of the polymers on the structure.

As can be seen from the foregoing, the modification of the properties of polymers by hexafluoroisopropylidene groups concerned many classes of polyheteroarylenes but polyimides have attracted most attention by investigators.[30,38] This can be explained to a considerable extent by the special place which polyimides occupy among polyheteroarylenes and also by the extensive possibilities for the modification of their structure by hexafluoroisopropylidene groups.

It is noteworthy that analysis of the "structure–properties" and especially "structure–solubility" relations is very difficult precisely for polyimides owing to the differences between the methods of their synthesis (thermal cyclisation of polyamidoacids or catalytic cyclisation of prepolymers in solution), the differences between their viscosity characteristics, etc.

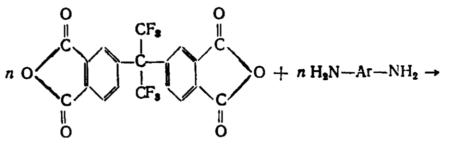
One of the first attempts at the modification of polyimides by hexafluoroisopropylidene groups concerns the synthesis of polypyromellitimide from 2,2-di(4-aminophenyl)hexafluoropropane[27] by a two-stage method:

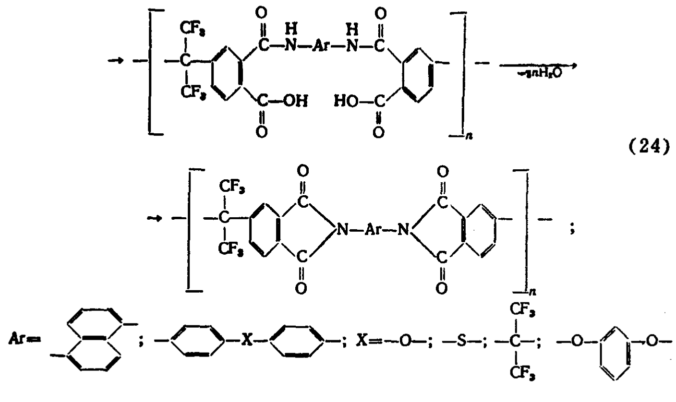


(23)

The polyimides obtained proved to be insoluble in organic solvents.

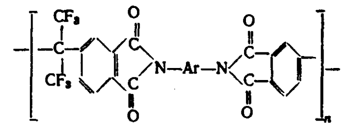
According to a series of data,[39–43] the polyimides based on the dianhydride of 2,2-di(3,4-dicarboxyphenyl)hexafluoropropane (dianhydride 6F) and various diamines are also soluble only in $SbCl_3$. They were obtained by a two stage method in accordance with the scheme

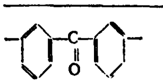
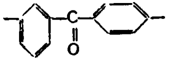
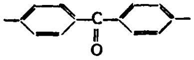
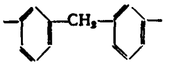
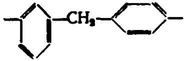
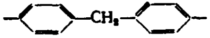
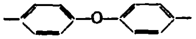



(24)

On the other hand, according to Clair et al.,[17] the polyimides containing hexafluoroisopropylidene groups are characterised in many instances by a satisfactory solubility in dipolar aprotic solvents (Table 3).

Table 3. Certain characteristics of polyimides having the general formula[17]



Ar	η^*_{log}	T_{soft}, °C	Solubility			
			N-MP	DMA	DMF	*m*-cresol
	0.47	260	+	+	+	±
	0.25	288	+	+	+	−
	0.35	311	−	−	−	−
	1.23	248	+	+	+	±
	0.86	272	−	−	−	−
	1.82	290	−	−	−	−
	2.20	307	−	±	+	+
	0.54	303	+	+	+	+
	0.90	339	+	+	+	+

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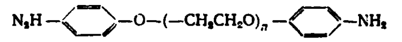
*The logarithmic viscosity (η_{log}) was determined in N-MP at 25 °C.

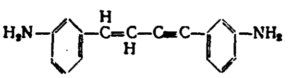
In the search for ways of increasing the solubility of the imides, investigators turned to the use of a diamine and a dianhydride containing in their molecules a combination of one hexafluoroisopropylidene group and two ether linkages, namely 2,2-di[(4-aminophenoxy)phenyl]hexafluoropropane[18] and the dianhydride of 2,2-di[4-(3,4-dicarboxyphenoxy)-phenyl]hexafluoropropane.[15,16,44-46] However, a significant increase of the solubility of the required polyimides could not be achieved by this procedure. Furthermore, an extremely detailed analysis of the relation between the structure of the polyimides based on asymmetric diamines and their solubility[17,47] showed that the polymers based on dianhydride 6F are much more soluble than the polyimides based on the same diamines and the dianhydride of 2,2-di[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane.[17] This at first sight anomalous phenomenon is probably associated with the greater content of hexafluoroisopropylidene units per conventional unit length of the macromolecule in polyimides based on dianhydride 6F. Certain characteristics of the polyimides based on dianhydride 6F and aromatic diamines with symmetrical and asymmetrical structures are listed in Table 3. In the analysis of the data in Table 3, the somewhat unexpected higher solubility of the polyimide based on dianhydride 6F and p-phenylenediamine compared with the polyimides based on dianhydride 6F and diamines such as 4,4'-diaminobenzophenone, di(4-aminophenyl)methane, and di(4-aminophenyl)ether has attracted attention. By analogy with the above, the explanation of the observed phenomenon is probably the greater number of hexafluoroisopropylidene units per conventional unit length of the macromolecule of the polyimide based on *p*-phenylenediamine.

Together with the traditional aromatic amines, systems with a more specific structure have been used in the synthesis of polyimides based on dianhydride 6F. The interaction of dianhydride 6F with diamines containing oligooxymethylene groups, having the general formula

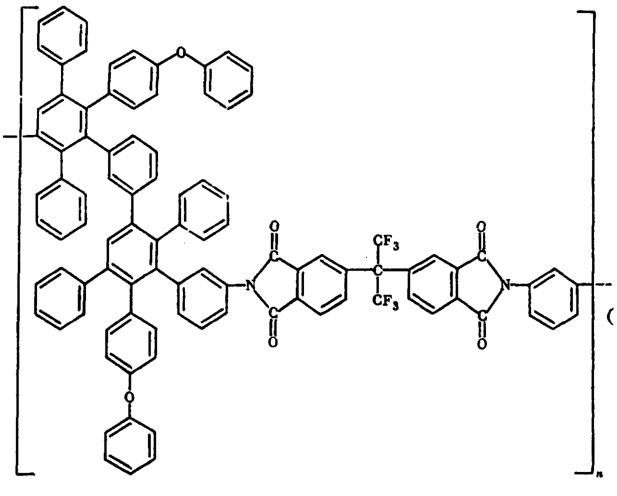

(25)

(n = 1,2,3,4), in *m*-cresol at 165–180 °C yielded polyimides which are soluble in chloroform and soften at 135–255 °C, depending on the structure of the diamine.[48,49]

A polyimide soluble in chloroform and dimethylacetamide (DMA) has been obtained under analogous conditions from dianhydride 6F and (*E*)-3,3'-(but-1-en-3-ynylene)dianiline:[44-46]


(26)

A polyimide having the formula


(27)

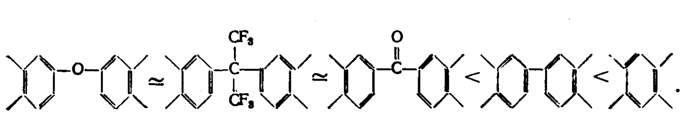
containing, together with hexafluoroisopropylidene groups, also 4-phenoxyphenyl and phenyl side groups which impart an improved solubility to rigid-chain monomers,[51] has been obtained[50] from dianhydride 6F. This polyimide is characterised by a glass point of 240 °C, is soluble in aromatic, chlorinated, and polar aprotic solvents, and retains 80% of its initial mass on thermal ageing at 343 °C for 200 h.[50]

The comparatively low softening temperatures of hexafluoroisopropylidene-containing polyimides make it possible to obtain from the low-molecular-weight polymers of this class articles with effective physicomechanical properties by cast moulding or extrusion.[42,52,53] The most promising polymers of this type—systems based on dianhydride 6F and aromatic diamines—are used by the Dupont Company as a basis for the development of binding or reinforced plastics[54–59] known by the name NR-150. According to Gibbs and Breder,[54] polyimides based on dianhydride 6F and various aromatic diamines are obtained by the chemical cyclisation of poly(*o*-carboxy)amides. The polymers obtained are soluble in pyridine, N-MP, and DMF. The glass points of the polyimides are in the range 229–385 °C, depending on the structure of the diamines. A low content of cavities (~1%) in the final materials is achieved by pressing at temperatures exceeding the glass points of the polyimides. Analogous pressing conditions are a precondition for success in the separation of glass plastics from solutions of poly(*o*-carboxy)amides. In all cases the presence of hexafluoroisopropylidene groups prevents the crystallisation of the polyimides. Glass plastics based on NR-150 have a tensile strength up to 3500 kg cm^{-2}, a modulus of elasticity of 2.24×10^5 kgf cm^{-2}, a static bending strength of 4900 kgf cm^{-2}, and a shear strength of 660 kgf cm^{-2}.[59] The most heat resistant of these systems can be used at 342 °C[54] and they retain 80% of their initial strength characteristics after ageing at 260 °C for 5000 h.[59]

Experiments with various polyimide binders have shown that NR-150 has the highest thermal stability and is most suitable for prolonged use in outer space.[59] Together with their employment as binders, such polyimide systems are of interest as adhesives and coatings.[60]

The positive effect of hexafluoroisopropylidene groups on the solubility of polyimides has been demonstrated also in relation to cardo-copolyimides with various microstructures synthesised using dianhydride 6F[61,62] and 2,2-di(4-aminophenyl)hexafluoropropane among various monomers.[62,63]

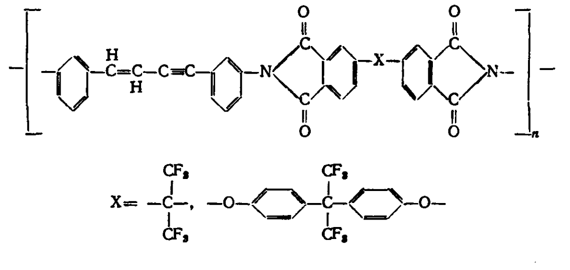
Comprehensive investigation of the properties of the copolyimides synthesised has shown that the introduction of hexafluoroisopropylidene groups tends to increase the solubility of the copolyimides. In terms of their influence on the softening temperatures of the polymers, the dianhydrides of tetracarboxylic acids can be arranged in the following sequence:[62]



(28)

The unique capacity of hexafluoroisopropylidene-containing oligo- and poly-heteroarylenes for being worked made them useful as thermoreactive polymeric systems. In recent years this field, which reduces to the creation of readily worked systems which are hardened after conversion into articles, has become one of the dominant fields in the chemistry of thermostable polymers. In particular, oligomers and polymers with ethynyl groups,[64] capable of cyclotrimerising with formation of trisubstituted phenyl intermolecular units, have attracted much attention. The ethynyl groups can be located in the main chains of the macromolecules, in the side substituents, and in the end groups of the oligo- and polyheteroarylenes. The use of reactive solvents and plasticisers, containing ethynyl groups and capable of participating, on hardening, in the formation of three-dimensional structures, proved to be extremely effective in a number of instances.

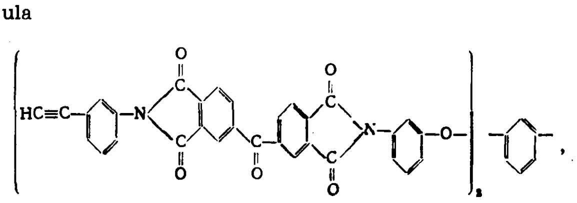
Each of the approaches enumerated above has been applied to some extent to hexafluoroisopropylidene-containing systems. Thus the introduction of ethynyl groups into the main chain of the macromolecule has been achieved in the synthesis of enyne polyimides:[44–46]



(29)

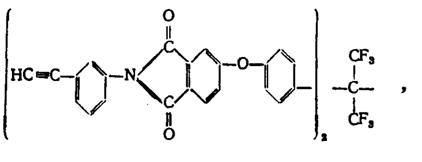
The hardening of these polymers at 265–316 °C led to the formation of "cross-linked" three-dimensional systems.

In order to make it easier to convert into finished articles the imidised oligomer Therimid-600, having the structural formula



(30)

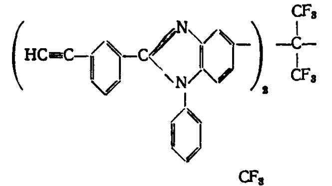
use was made of the reactive plasticiser



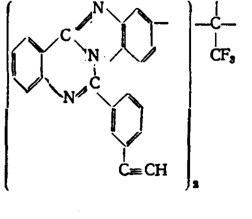
(31)

obtained by the reaction of the dianhydride of 2,2-di[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane [Scheme (8)] with 3-ethynylaniline.[64]

Finally, bis(*N*-phenylbenzimidazole)[65] and bisbenzimidazoquinazoline[66] with ethynyl end groups, i.e.



(32)



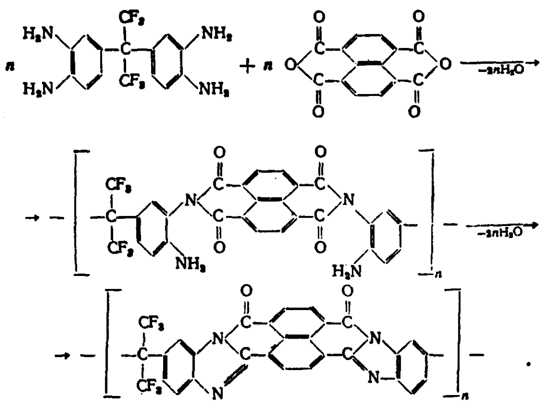
(33)

were converted into thermostable three-dimensional products by thermal polycyclotrimerisation.[64]

The extremely successful use of hexafluoroisopropylidene groups for the improvement of the "workability" of the traditional polyheteroarylenes led Korshak and co-workers to take the next step, namely to attempt the modification of "ladder" polyheteroarylenes by hexafluoroisopropylidene groups. The choice of these systems was dictated by the fact that many ladder systems have high thermal stabilities and heat resistances but are extremely difficult to work with and to convert into articles.[67–71]

The hexafluoroisopropylidene-containing ladder polyheteroarylenes were investigated within the framework of the synthesis of polynaphthoyleneazoles, namely polynaphthoylenebenzimidazoles and polynaphthoylene-*sym*-triazoles, which are the products of the three-stage reactions of bis(naphthalic anhydrides) with tetrafunctional aromatic nucleophiles [bis(*o*-phenylenediamine) and bisamidrazones of dicarboxylic acids][67] and also polybenzimidazoquinazolines and polybenzo(dipyrimidobenzimidazoles), which were obtained in two stages, by the reaction of diamines, containing benzimidazole rings in the *o*-positions relative to the amino-groups, with derivatives of aromatic dicarboxylic acids.[69–71]

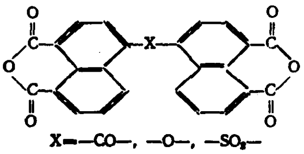
In the course of studies on hexafluoroisopropylidene-containing polynaphthoylenebenzimidazoles, a polymer was developed on the basis of 2,2-di(3,4-diaminophenyl)hexafluoropropane and the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid.[72–75] It was synthesised in accordance with the scheme



(34)

The reaction was carried out in phenolic solvents—*m*-cresol and phenol—using benzoic acid as the catalyst.[76] This made it possible to synthesise the polymer under comparatively mild conditions (at 180 °C). The reaction, occurring under homogeneous conditions, led to the formation of high-molecular-weight polynaphthoylenebenzimidazole with a degree of cyclisation close to 100%.[72–75] The polymer obtained dissolves not only in acid but also in phenolic solvents (*m*-cresol and a mixture of phenol and tetrachloroethane). Films with a tensile strength of 980 kg cm^{-2} at 25 °C and a 60% elongation on rupture, retaining satisfactory deformation-strength characteristics up to 380 °C, have been obtained from such solutions by casting.

In order to increase further the solubility of polynaphthoylenebenzimidazoles, the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid was replaced in reaction (33) by the dianhydrides of carbonyl-, oxy-, and sulphonyl-bis(naphthalic acids):[77–82]



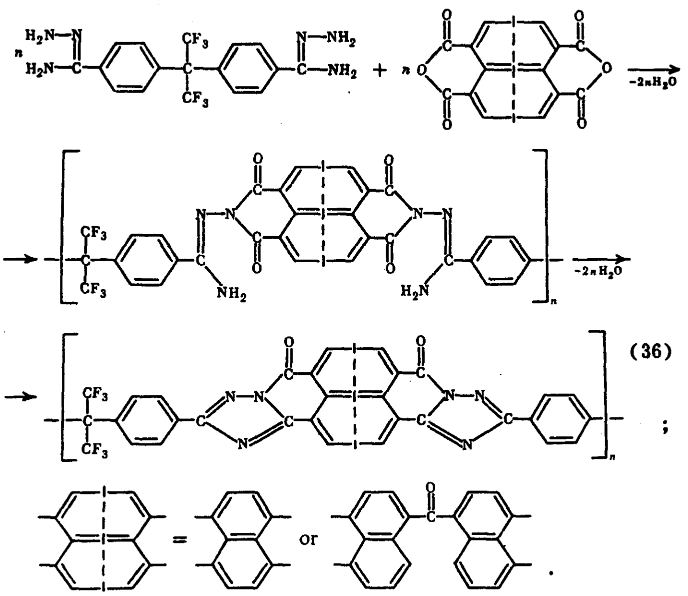
(35)

$X = -CO-,\ -O-,\ -SO_2-$

The resulting polynaphthoylenebenzimidazoles, containing alternating hexafluoroisopropylidene and other "bridging" groups, dissolve not only in phenolic solvents but also in hot N-MP. However, one should note that these polymers had very low viscosities ($\eta_{int} \approx 0.3$ dl g^{-1}), which precludes unambiguous conclusions about the influence of their structure on the solubility.

Overall, polynaphthoylenebenzimidazoles with hexafluoroisopropylidene groups, in the first place the polymer based on 2,2-di(3,4-diaminophenyl)hexafluoropropane and the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid, are of undoubted interest and, provided that the problem of the starting materials can be solved, their use may extend outside the framework of academic research.

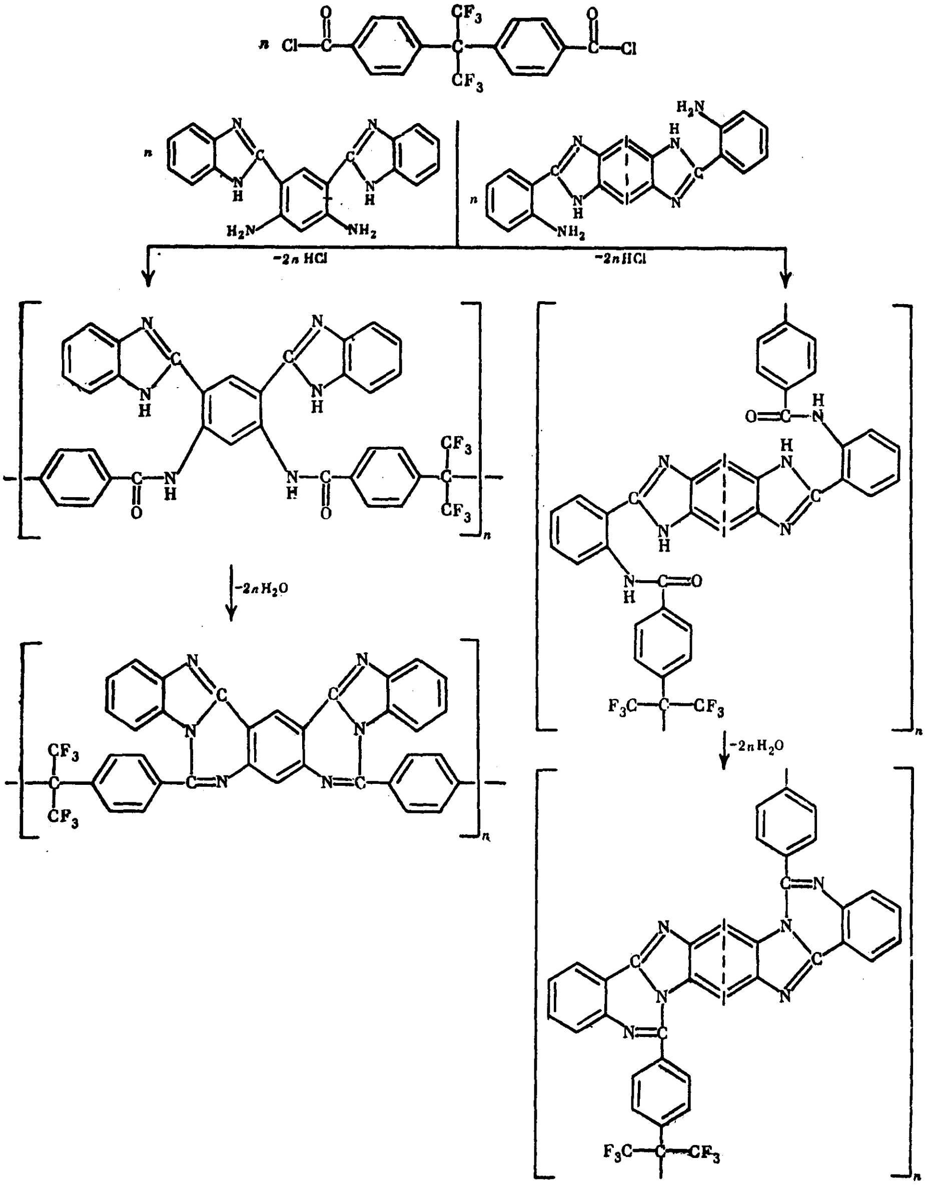
Together with polynaphthoylenebenzimidazoles, polynaphthoylene-*sym*-triazoles, which are the products of the interaction of the bisamidrazone of 2,2-di(*p*-carboxyphenyl)hexafluoropropane with bis(naphthalic anhydrides), attracted the attention of the same group of investigators:[83,84]



(36)

Polynaphthoylene-*sym*-triazoles were synthesised[83,84] under conditions identical to those used to obtain polynaphthoylenebenzimidazoles; high-molecular-weight polymers soluble in phenolic solvents and having softening temperatures in the range 380–420 °C with oxygen indices of 43–46 were obtained.

In order to synthesise polybenzimidazoquinazolines and polybenzo[di(pyrimidobenzimidazoles)] containing hexafluoroisopropylidene groups,[85–89] bis[2(2-aminophenyl)6-benzimidazoles] and 1,3-di(2-benzimidazolyl)-4,6-diaminobenzenes were made to react with the dichloride of 2,2-di(*p*-carboxyphenyl)hexafluoropropane [Scheme (37)].



(37)

The reactions were carried out under the conditions of a two-stage process; the first stage was performed at room temperature in N-MP in hexamethylphosphoramide and the second in the solid phase at 350–380 °C. The resulting polybenzimidazoquinazolines and polybenzo[di(pyrimidobenzimidazoles)] dissolved only in H_2SO_4 and CF_3COOH, but it is not clear whether this is a consequence of the severe conditions in the cyclisation processes or of the chemical structure of the polymers.

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Analysis of the data presented in the review shows that the introduction of hexafluoroisopropylidene groups into the main chains of the macromolecules constitutes an effective method of imparting an improved solubility, an improved fire resistance, and also elasticity to rigid-chain polymers. Provided that the starting materials can be obtained, this field may prove to be promising for the preparation of polymers with a valuable set of properties.

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Chromatographic Separation of Glucose and Fructose

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The structures, mutarotation, and the physicochemical properties of glucose and fructose as well as methods for their separation are examined. Their chromatographic separation on cation exchangers in the calcium-form is discussed in detail. A theory of the formation of complexes of carbohydrates with metal cations is described and the mechanism of the separation of glucose and fructose on cation exchangers in the calcium-form is discussed in detail. Factors influencing the chromatographic separation of glucose and fructose on sulphonic acid cation-exchange resins are also considered.
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I. INTRODUCTION

The technology used previously (up to the middle 1970's) in the preparation of fructose was based on the application of a scarce and expensive raw material—inulin, which is a fructose polymer. This prevented the wide-scale use of fructose in the food and medical industry. Only in the last decade the application of chromatographic methods permitted the large-scale manufacture of fructose by its isolation from glucose-fructose syrups obtained either as a result of the inversion of sucrose or by converting glucose with the aid of glucose isomerase.

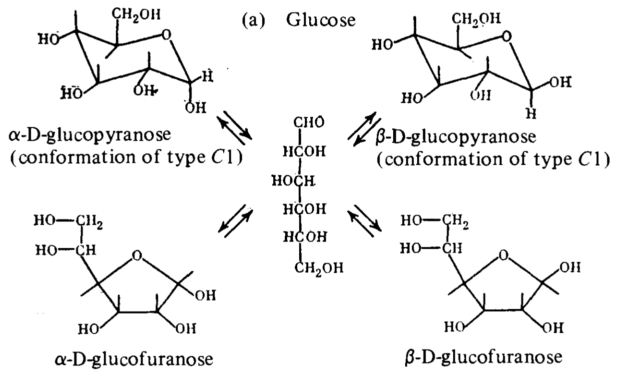
The industrial manufacture of fructose based on the chromatographic separation of glucose-fructose syrups on cation-exchange resins in the calcium-form has already been approved in some countries. The Suomen Sokeri Company [the Finnish Sugar Company] (Finland) is the largest manufacturer of fructose in the world. Its factories in Finland and the USA manufacture about two-thirds of the entire fructose produced throughout the world, i.e. 20000 tonnes annually. France occupies the second place in the manufacture of fructose and is followed by the Federal Republic of Germany and Austria.[1]

In connection with the active development of the technology for the preparation of fructose on the basis of chromatographic methods, it is important to know the properties and characteristics of the behaviour of glucose and fructose under various conditions and also the mechanism of their chromatographic separation.

II. THE STRUCTURES AND PROPERTIES OF GLUCOSE AND FRUCTOSE

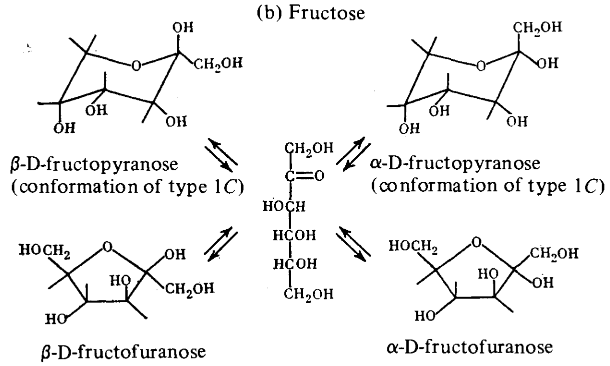
Glucose and fructose mutarotate in solution, which leads to the establishment of equilibrium between five structural forms of each of these compounds, as shown in Scheme 1:

Scheme 1



(a) Glucose

(b) Fructose



The composition of the equilibrium mixture is influenced primarily by the nature of the solvent and temperature. In the case of D-glucose, the equilibrium mixture in aqueous solution at 20 °C consists of 63.8% of β-D-glucopyranose, 36.2% of α-D-glucopyranose, and trace amounts (0.0026%) of the open-chain acyclic structure.[2,3]

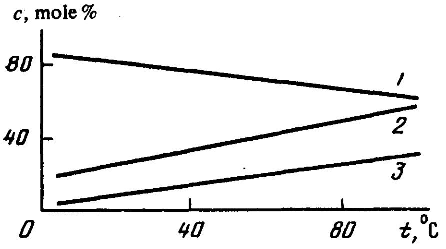
The following equilibrium composition has been established for D-fructose in aqueous solution at 20 °C: 76.4% of β-D-fructopyranose, 19.5% of β-D-fructofuranose, and 4.1% of α-D-fructofuranose.[4]

An increase of temperature leads to a linear increase of the content of fructofuranoses and a corresponding decrease of the content of β-D-fructopyranose.[5] For example, at 0 °C the equilibrium aqueous solution of D-fructose contains 84.8% of β-D-fructopyranose, 11.1% of β-D-fructofuranose, and 4.1% of α-D-fructofuranose, while at 50 °C the corresponding proportions are 55.8, 31.9, and 12.3% respectively.[6]

These data agree with the temperature dependence of the equilibrium composition of a solution of D-fructose in water obtained by Shallenberger[7] (see Figure). Equations permitting the calculation of the content of each form of D-fructose in aqueous solution as a function of temperature t are quoted in the same communication:

$$c_1 = -0.48t + 86.72 \ ,$$
$$c_2 = 0.26t + 14.32 \ ,$$
$$c_3 = 0.23t - 0.55 \ ,$$

where c_1, c_2, and c_3 are the contents of β-D-fructopyranose, β-D-fructofuranose, and α-D-fructofuranose respectively (in mole %).



Temperature dependence of the equilibrium composition of D-fructose in aqueous solution: 1) β-D-fructopyranose; 2) β-D-fructofuranose; 3) α-D-fructofuranose.[7]

The specific rotation of the equilibrium mixture of D-fructose at a temperature t can be calculated from the formula[7]

$$\alpha_D^t = 0.56t - 102.6 \ .$$

The rate of mutarotation is higher the higher the temperature. At 20 °C in aqueous solution the mutarotation process virtually terminates after 20 min.[4]

The temperature dependence of the equilibrium composition of D-glucose has a somewhat different character than for D-fructose. The contents of α-D-glucopyranose and β-D-glucopyranose are respectively 36 and 64% at temperatures ranging from 5° to 30 °C, while at 80 °C the contents are 46 and 54%.[3,8] Unfortunately there are no literature data on the ratios of glucopyranoses in the temperature range 30–80 °C.

The concentration in aqueous solutions of both glucose and fructose has almost no influence on the equilibrium composition; only a weak tendency towards an increase of the content of α-D-glucopyranose with increasing concentration of D-glucose in aqueous solution has been observed, at least in the concentration range from 5 to 65%.[8,9] Similarly, the increase of the concentration of D-fructose from 5 to 80% entails a slight decrease of the fraction of β-D-fructopyranose and the corresponding increase of the content of fructofuranoses.[9,10] The above trends lead to a difference between the equilibrium compositions of D-glucose and D-fructose by only 3–4%.

The fractions of all the forms present in solution depend on their relative free energies. The "chair" form, in which the anomeric OH group is in the axial position, i.e. the 1C conformation, is more stable for D-fructose.[11,12] β-D-Fructopyranose has this conformation also in the crystalline state. In general the furanose form in which the O(2) and O(3) atoms are in the *cis*-positions is more stable for any ketohexose. In this case the interaction between O(3) and the hdyroxymethyl group is weakened. For this reason, the β-D-fructofuranose form of D-fructose, present in aqueous solutions in greater amounts than the α-D-fructofuranose form, is more stable. The stability of furanoses increases in solution in dimethyl sulphoxide (DMSO), while pyranoses are more stable in water.[12]

The composition of the D-fructose equilibrium mixture at 20 °C is presented in the Table as a function of the nature of the solvent. It permits the conclusion that the content of fructopyranoses increases, while that of fructofuranoses diminishes with increasing solvent polarity. This is partly associated with the hydration of the hydroxy-groups, because the large solvated groups are subject to less steric hindrance when the carbohydrate exists in solution in the form of pyranose in the "chair" conformation and not in the form of the furanose ring. In non-aqueous solvents, this effect is less important, because solvation in such solvents cannot be quite so appreciable as in water, the hydroxy-group occupies a smaller volume, and the advantages of the pyranose conformations compared with the furanose conformations diminish.[14]

The influence of the nature of the solvent on the composition of the equilibrium D-fructose mixture at 20 °C.

Solvent	Content, mole %		
	pyranoses	furanoses	refs.
Dimethyl sulphoxide	18.5	81.5	[12]
Ethanol (90%) + water (10%)	43	57	[2]
Ethanol (80%) + water (20%)	49	51	[2]
Pyridine*	53	42	[13]
Water	76	24	[4.12]

*The solution in pyridine contains 5% of the keto-form.

The majority of aldopyranoses, including glucopyranose, exist in aqueous solution in a conformation of type C1, because it is energetically more favourable. For example, the free energy of the C1 conformation of α-D-glucopyranose is 2.4 kcal mol^{-1}, while the energy of the 1C conformation is

6.55 kcal mol^{-1}; in the case of β-D-glucopyranose, the free energies of these conformations are 2.05 and 8.0 kcal mol^{-1} respectively.[15] Thus the type *C*1 conformation predominates for D-glucose (see Scheme 1).

The free energy of α-D-glucopyranose is somewhat higher than that of β-D-glucopyranose owing to the axial disposition of the anomeric OH group. For this reason, a smaller amount of α-D-glucopyranose (36%) is observed in aqueous solution compared with β-D-glucopyranose (64%), in which all the OH groups are equatorial.[2] In aqueous solutions D-fructose exists in a type 1*C* conformation[12] (Scheme 1).

The equilibrium aqueous solution of D-glucose has α_D^{20} = +52.7°, while for the D-fructose solution under the same conditions we have $\alpha_D^{20} = -92.4°$.[16]

D-Glucose and D-fructose are monosaccharides, which readily undergo chemical changes. Under the influence of bases, they undergo isomeric interconversion via the intermediate enol, accompanied by the formation of mannose. Thus a mixture of D-glucose, D-fructose, and D-mannose is obtained from D-glucose in a very dilute solution of alkali.[14] In aqueous alkaline solutions at higher pH (pH ≥ 9), the sugar forms a complex with the alkali, which is followed by alkaline transformation and decomposition.[17] In a study[18] of the kinetics of the decomposition of fructose and glucose in an alkaline medium on heating, it was noted that fructose decomposes appreciably faster than glucose.

In general, fructose is chemically much less stable than glucose. Thus heating of an alkaline solution of D-fructose at pH 8 and 80 °C for 20 min leads to the development of an appreciable yellow colour in solution and, as the pH is raised, the intensity of the colour rises rapidly.[19]

The study of the transformation of sugars in solution in pyridine showed that the double bond can migrate via the enediol mechanism along the entire carbon chain. The same mechanism constituted the basis of a wide variety of reactions of monosaccharides, in particular their cleavage by strong acids and bases.[20] Glucose and fructose, especially glucose, are very resistant to the action of acid. Thus, under mild conditions, the interconversion of the sugars is possible, while under severe conditions dehydration, leading to the formation of furfural and related compounds, takes place.

Heating of D-glucose in dilute sulphuric acid solution at 100 °C leads to the formation of D-fructose, D-arabinose, and small amounts of D-mannose and D-xylose. Under the same conditions, fructose undergoes the aldose–ketose isomerisation.[21]

The products of the conversion of D-glucose by various dilute acids are D-fructose, D-mannose, isomaltose, gentiobiose, etc. The mixture composition depends on the nature of the catalyst employed.[22] Analogous results have been obtained in another study,[23] where, however, it was emphasised that oligomers are formed only in 10% solution of glucose when a 0.01–0.2 *N* solution of hydrochloric acid is used.

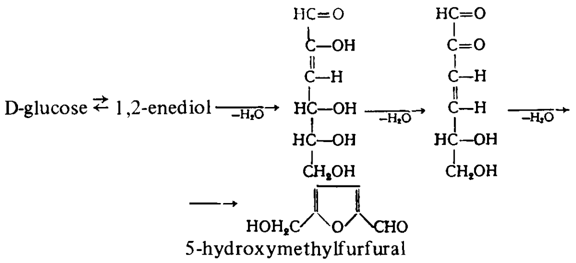
Under more severe conditions, the dehydration becomes the dominant process. The dehydration of hexoses in an acid aqueous medium leads to the formation of not only 5-hydroxymethylfurfural but also of 2-hydroxyacetylfuran.[24] In addition difuryl ether may be formed.[25]

Fructose undergoes condensation in an acid medium mainly at moderate temperatures (~60 °C) and pH 1.3–3.5 with formation of levanbiose, inulobiose, and other products.[26] At pH ≥ 3.9, D-fructose is dehydrated without the formation of 5-hydroxymethylfurfural, while at pH > 4.5 it isomerises to D-glucose.[27]

Thus the conversion of glucose and fructose in alkaline and acid media can result in the formation of a wide variety of products whose composition depends on the pH of the medium, the reaction time, temperature, the nature of the catalyst, and the concentrations of the monosaccharide and catalyst.

The dehydration of D-glucose on heating in aqueous solution can be described by the scheme[28]

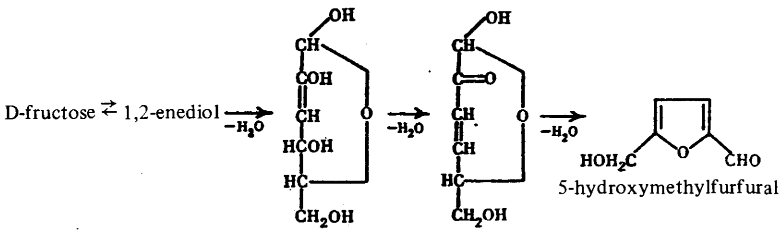
Scheme 2



A 2,3-enediol, which is ultimately converted into 2-hydroxyacetylfuran, can also be formed from D-glucose.

Dehydration of D-fructose on heating in aqueous solution can be described by the scheme[29]

Scheme 3



D-Fructose reacts chemically extremely readily, which has been demonstrated by Shamgar and Leibowitz.[30] After D-fructose has been kept in absolute ethanol at room temperature for some time, methylglyoxal, difructosoanhydrides, diheterolevulosans, β-methyl fructopyranoside, and two glucose derivatives are detected in solution after a time. Thus, under these conditions, D-fructose undergoes anhydridisation, isomerisation, dimerisation, and decomposition into fragments, each containing three carbon atoms. D-Glucose undergoes no changes whatever under the same conditions.[30]

In a cold aqueous solution, fructose is 1.6 times sweeter than sucrose; however, in hot aqueous solution the sweetness of fructose diminishes appreciably. It has been shown[2,4] that the sweetness of fructose depends on the ratio of the tautomeric forms. Fructofuranoses have almost no sweet taste, the carrier of which is in fact β-D-fructopyranose. If the sweetness of sucrose is assumed to be 100%, then that of β-D-fructopyranose is 180–200% and that of fructofuranoses is 0%. The sweet taste of β-D-fructopyranose is determined by the presence of three-component groups incorporating the anomeric hydroxy-group, the oxygen atom in a primary alcoholic group, and the ring methylene carbon atom.[31] Since it has been shown[7] that the amount of β-D-fructopyranose diminishes with increase of temperature and is accompanied by the corresponding increase of the amount of furanoses, the weakening of the sweet taste of fructose in a hot aqueous solution becomes understandable.

III. METHODS OF SEPARATION

There exist many methods for the separation of glucose–fructose mixtures. It is possible to distinguish five main groups of methods.

1. Methods based on dialysis using ion-exchange membranes.[32,33] These methods require the application of very complex equipment and also the expenditure of much electrical energy.[33] For this reason, they are extremely expensive.

2. Methods based on chemical reactions with one of the mixture components (glucose or fructose). Here use is made of the oxidation of glucose to gluconic acid with subsequent precipitation of the latter by calcium salts and its removal from fructose solution,[34,35] the formation of hydrazones from one of the sugars and their subsequent hydrolysis,[36,37] the interaction of the sugars with metal carbonyls and subsequent hydrolysis of one of the resulting products,[38] the formation of chemical compounds of phenol-containing resins with glucose,[39] etc. The fructose obtained by these methods requires careful purification and glucose, which is a valuable sugar, is converted into waste.

3. Methods based on the differential crystallisation of glucose and fructose. Many such methods exist. For example, the following procedures are used: cooling of the invert syrup with subsequent introduction of glucose seed crystals, the crystallisation of glucose, and its separation from the fructose solution;[40] the formation of a complex of glucose and sodium chloride, which crystallises from the solution;[41] preliminary differential crystallisation of glucose and fructose with subsequent separation on a cation exchanger;[42] differential crystallisation in methanol using the difference between the crystallisation temperatures of glucose and fructose.[43,44] However, completely pure glucose and fructose cannot be obtained by these methods.

4. Methods based on the isolation of fructose in the form of complexes with a calcium compound, for example $Ca(OH)_2$ [45–47] or $CaCl_2$.[48–52] These methods are relatively ineffective owing to the low yield of the final product (10–20%).

5. The group of ion-exchange chromatographic methods, which can be in its turn subdivided into three main subgroups:

(a) Chromatographic separation of glucose and fructose on zeolites, including zeolite X, containing K^+ cations and capable of selective adsorption of glucose;[53–56] on a zeolite containing NH_3^+, K^+, Na^+, Ca^{2+}, and Ba^{2+} cations and capable of the selective adsorption of fructose;[57] on zeolites X, Y, or L containing the Li^+, Na^+, K^+, Cs^+, Be^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, etc. cations[58–60] and also on a mineral adsorbent of the "Sorbex" type.[61]

(b) Separation of glucose and fructose on anion-exchange resins. The separation is usually carried out at 40–60 °C on anion-exchange resins, usually of the Dowex I type, in the bisulphite- or sulphite-form, using water as the eluent.[62–72] However, the employment of an anion exchanger in the above forms results in the presence of SO_3H^- and SO_3^{2-} ions in the glucose and fructose obtained, because these are readily eluted by water.[65] In order to avoid the presence of these impurities, it is necessary to employ additional purification columns with the anion exchanger in the OH-form, which entails additional dilution of the sugar solutions. A mixture of an anion exchanger in the bisulphite-form with 5% of a cation exchanger in the sodium- and hydrogen-forms has been used,[77] which made it possible to improve the separation of the glucose–fructose mixture.

(c) The separation of glucose and fructose on cation-exchange resins. Sulphonated polystyrene resins cross-linked by divinylbenzene (DVB) and containing alkali metal or alkaline earth metal cations are usually employed. Other forms are also used. When glucose and fructose were separated on the Dowex 50 × 4 cation-exchange resin in the Ba-form, the glucose and fructose peaks were found to be markedly diffuse, on the Ag-form a weak separation was observed, while on the Sr-form a fairly effective separation was achieved.[78] The use of the sodium-form of the cation exchanger[79] does not allow the separation of the glucose-fructose mixtures, but partial separation of mono-, di-, and tri-saccharides was noted. Comparison of the efficiencies of the various forms of cation-exchangers leads to the conclusions that the Ca^{2+} cation is most suitable for the separation of glucose and fructose. The same conclusion follows from the study of Mountfort.[80]

Cation-exchange resins in the Ca-form with a degree of cross-linking equivalent to 2–8% of DVB are used in most studies.[81–97] The eluent is water, the separation is carried out at 50–70 °C, and the concentration of the syrup introduced amounts to 50% and above in terms of the dry substances. The resin is normally employed in the form of 0.2–0.5 mm beads and an attempt is made to employ as narrow a fraction as possible. An important factor, which influences the efficiency of the chromatographic separation, is the density and uniformity of the packing of the resin bed in the column. A study[98] has been devoted to this question and a method has been proposed whereby a dense packing of the resin in the Ca-form with a bead size of 0.3–0.6 mm can be achieved. It is based on the ability of sulphonated polystyrene resins to swell in a concentrated $CaCl_2$ solution (20%) to a lesser extent than in water. A suspension of the resin in calcium chloride solution is supplied into the column and the resin is then washed with water.

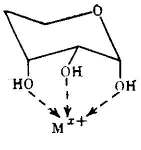
Cation-exchange resins of the Dowex 50 type have been used,[81–98] but other cation exchangers, for example Duolite C 20 × 4,[99] Amberlite IR-120B,[100] Permutit Q,[111] and Duolite C 25[102] have also been employed in the calcium-form under conditions analogous to those indicated above.

Semicontinuous processes have been used in a number of investigations[103–107] for the separation of glucose and fructose: the "modelled moving bed" method[103] on a sulphonic acid cation-exchange resin in the Ca-form; the "fluidised bed" method[104] on a strongly acid cation-exchange resin in the Ca-form; the "cyclic zonal separation" method[105] on an aminoethylcellulose derivative; the "moving inlet" method[106] on a cation-exchange resin in the Ca-form. A procedure has also been developed in which use is made of a column containing alternating reaction and adsorption zones.[107] Glucose then isomerises in the reaction zone to fructose, which is adsorbed in the adsorption zone.

IV. PHYSICOCHEMICAL ASPECTS OF THE CHROMATOGRAPHIC SEPARATION OF GLUCOSE AND FRUCTOSE

Fructose, glucose, sucrose, and other carbohydrates form 1:1 molecular complexes with bases. Reducing sugars, which include glucose and fructose, give rise to more stable complexes than non-reducing sugars, for example, sucrose.[108–110] Metal cations have different complex-forming capacities, which depend on their valence and size. Thus, according to Dangre,[111] univalent metal cations can be arranged in the following sequences in terms of their complex-forming capacities: $Na^+ > K^+ > Li^+$ for glucose and $K^+ > Na^+ > Li^+$ for fructose. The sequences of bivalent cations are as follows: $Sr^{2+} > Mg^{2+} > Ca^{2+} > Ba^{2+}$ for glucose and $Ca^{2+} > Sr^{2+} > Ba^{2+} > Mg^{2+}$ for fructose. However, not all carbohydrates form complexes with cations in aqueous solution and the complexes themselves have different stabilities. It has been possible to demonstrate by NMR and electrophoretic methods that complex formation with metal cations is possible in the presence of three OH groups in favourable steric positions. This situation arises when three neighbouring OH groups are arranged in the sequence axial–equatorial–axial (*a–e–a*).[112–115]

On the basis of NMR and electrophoretic data, Goulding proposed in 1975[116] his theory of the formation of complexes of carbohydrates with metal cations. The most stable complexes are formed in the presence of the *a–e–a* sequence of three neighbouring OH groups in the pyranose ring or the *cis,cis*-sequence of three OH groups in the furanose ring:



a–e–a

The stability constants K_S of such complexes are in the range 1–5 $mole^{-1}$. $K_S = 0.1\ mol^{-1}$ for the *a–e*(*cis*) sequence. The *e–a–e* sequence gives rise to a less stable complex. Finally the *e–e* sequence is even less favourable than the *a–e* sequence and complexes are not formed at all for the *a–a* sequence. Hence follows an important conclusion: the greater the number of favourably oriented pairs of OH groups in the carbohydrate molecule, the more stable the complexes. For example, α-D-glucopyranose and α-D-fructopyranose each have one pair of OH groups in the *a–e* sequence, β-D-fructopyranose has two pairs, while β-D-glucopyranose has no such pairs.

In relation to allose, it has been demonstrated[112] that the complexes of furanoses are always less stable than those of pyranoses.

The optimum radius of the cation for complex formation is ~1.0 Å. The greater the charge of the cation, the easier the formation of the complex: the sizes of Na^+, Ca^{2+}, and La^{3+} are 0.97, 0.99, and 1.02 Å respectively.[112]

It follows from the data of Goulding,[116] who determined the capacity coefficients of sugars (k') on the Aminex A-5 cation-exchange resin with a particle size of 11 ± 2 μm using different cations, that fructose forms fairly stable complexes with K^+, Ag^+, Tl^+, and Ca^{2+} and slightly less stable complexes with Sr^{2+}. On the other hand, on the cation exchanger containing the K^+, Ag^+, and Tl^+ cations, the values of k' for glucose are also fairly high, which means that, when these cations are employed, it is not possible to achieve a satisfactory separation of glucose–fructose mixtures. Since strontium is toxic, one may conclude that the most suitable cation for the selective complex formation with fructose in the presence of glucose is that of calcium.

The mechanism of the separation of glucose and fructose is most probably based on the presence in β-D-fructofuranose of two *cis*-OH groups attached to the five-membered ring.[117] The two pairs of OH groups in the *a–e* sequence in β-D-fructopyranose have hardly any significant influence on the separation, because they can ensure the formation of only very weak complexes with the cation. Glucose, for which only α-D-glucopyranose among all the possible isomers has one pair of OH groups in the *a–e* sequence, forms an even weaker complex. In the course of separation on the column, the sugars mutarotate. The binding of β-D-fructofuranose to calcium shifts the mutarotation equilibrium in the liquid phase. The faster this process, the narrower the peak of the fructose eluted.

An analogous phenomenon takes place also with glucose. Under favourable conditions, where the mutarotation is slow, the glucose and especially fructose peaks can be appreciably diffuse, which can be explained by the fact that β-D-glucopyranose is eluted initially, is followed by α-D-glucopyranose, then β-D-fructopyranose, and finally β-D-fructofuranose. The available data, demonstrating an appreciable narrowing of the carbohydrate peaks with increase of temperature, may serve as confirmation of this finding.[83,84,118] In the case of fructose, an increase of temperature accelerates the mutarotation process itself in the first place and shifts the equilibrium towards furanose in the second place.[7] However, another factor then begins to operate—the stability of the complex of fructose with the cation; an increase of temperature diminishes the stability of the complex. In order to achieve the optimum separation, it is essential to select a temperature at which the optimum combination of the stability of the complex, the rate of mutarotation, and the composition of the initial equilibrium mixture is achieved. Furthermore, there are other factors, which will be described below.

The presence of H^+ and also OH^- ions sharply accelerates the mutarotation and also facilitates the separation of glucose and fructose.[92] It is of interest to note that, when the cation exchanger is converted into the calcium-form by a standard method with a 10% solution of calcium chloride, part of the resin is bound to remain in the H^+-form (3–5%). If the resin is fully converted into the Ca-form (and this is possible at an elevated temperature or when an alkaline solution of calcium chloride is used), then the separation of glucose and fructose is impaired. This demonstrates the possibility of mutarotation processes in chromatographic columns. Apart from the H^+ and OH^- ions, triethyl- and trimethyl-amines cause a sharp acceleration of the mutarotation. The addition of very small amounts of triethylamine to the eluent (water) narrows the fructose and especially glucose peaks.[119] The effect of triethylamine can apparently be explained by the fact that it makes the solution weakly alkaline and this accelerates sharply the mutarotation.

It has also been noted that the stability of the complexes of sugars with metal cations is influenced by the nature of the eluent. The stability constants of the complexes in ethanol are known to be appreciably higher than in water;[120,121] however, owing to the similarity of the partition coefficients of glucose and fructose, it is usually not possible to achieve their satisfactory separation in ethanol.

The employment of anion-exchange resins for the separation of glucose–fructose mixtures leads to undesirable transformations in the individual sugars.[122,123] The decomposition of glucose and fructose with formation of glycolic and citric acids is actually observed on strongly basic anion-exchange resins, for example on Amberlite IRA-400.[124]

The decisive process in chromatography on granular materials, including cation-exchange resins, is diffusion of the sugar within the resin particles,[125] which depends in its turn on the flow rate of the mobile phase, temperature, the resin grain size, the degree of cross-linking of the resin, and the nature of the solvent and the sugar.

An increase of temperature accelerates the diffusion,[126] but, since it entails the narrowing of the peaks of the components separated, it does not always improve the separation of the mixture, since k' diminishes at the same time.[127] On the other hand, at low temperatures sugars are adsorbed more strongly and the resolution can therefore be improved, provided that the influence of the decrease of the rate of mass transfer is small and the influence of mutarotation is suppressed.[119] It has been noted[117,128] that a decrease of temperature improved the separation of glucose and fructose on a cation-exchange resin in the Ca-form.

One of the important factors in the chromatographic separation of sugars is the flow rate of the mobile phase. It is limited by the diffusion of sugars within the resin particles.[129–131] At a high flow rate of the mobile phase, the peaks of the substances being separated become asymmetric, and long "tails" appear, their presence being explained by the fact that a proportion of the sugars continue to diffuse from the resin particles into the mobile phase.

A decrease in the resin particle size increases the rate of mass transfer. For example, the change in the bead size of the Dowex 21(K) resin from 45–75 to 15–40 μm improved the separation of glucose, sucrose, and raffinose by a factor greater than 3, causing a sharp narrowing of the peaks of the test substances.[129] The greater efficiency of the Dowex 50 × 8 cation-exchange resin in Ba-form[132] compared with the Ca-form[133] can be explained by the smaller size of the resin particles employed in the former case (0.038–0.075 mm compared with 0.15–0.30 mm). A relation between the cation exchanger bead size and the yield of pure fructose has been observed:[134] the smaller the bead size, the greater the yield. Furthermore, the employment of narrower resin bead fractions causes an additional improvement in the separation of the test substances, which is apparently largely related to a more uniform packing of the beads in the bed. The use of a resin with a large bead size necessitates the employment of very low flow rates of the mobile phase, owing to the low rate of mass transfer in the large resin beads, and precludes the attainment of a satisfactory separation of the glucose–fructose mixture.[135]

Since sugar molecules have a complex steric configuration and in order to achieve complex formation with the active centre of the cation exchanger they must assume a definite position which ensures the formation of bonds of approximately equal length between the metal and the complex-forming OH groups of the carbohydrate,[114,136] it is clear that the steric structure of the cation-exchange resin must influence the chromatographic separation. The steric structure of the cation exchanger is in its turn determined by the degree of cross-linking. The degree of cross-linking of the cation exchanger must not exceed a definite limit.[79,84,88,90,92,101,137] On the other hand, analysis of the above studies leads to the conclusion that the degree of cross-linking should not be below a definite limit. The most favourable conditions are apparently ensured by a degree of cross-linking by DVB of 4–8%. The use of cation-exchange resins with a lower degree of cross-linking, for example of the KU-2-2(Ca) cation-exchange resin, in which the degree of cross-linking is 2%,[138] has been shown to[137] lower the efficiency of the separation of glucose and fructose. The causes of this are not altogether clear, but the main deficiency of cation-exchange resins with a low degree of cross linking (2% of DVB and below) is their low mechanical strength.

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Thus, in devising various technologies for the manufacture of fructose, based on chromatographic methods for the separation of glucose–fructose mixtures on cation-exchange resins, account must be taken of several most important factors.

Firstly, glucose and especially fructose are chemically extremely unstable carbohydrates and any operations with these sugars require mild conditions (pH 5–7, temperature ≤60 °C). Secondly, calcium cations are the most suitable for the selective complex formation with fructose in the presence of glucose and the mechanism of their separation on cation-exchange resins in the Ca-form is most likely to be based on the formation of a relatively stable complex of β-D-fructofuranose with calcium. Thirdly, the degree of cross-linking of the cation-exchange resin, equivalent to 4–8% of DVB, apparently ensures the optimum separation of glucose and fructose. Finally, when the cation-exchange resin is treated with a solution of calcium chloride, an attempt to achieve its conversion into the 100% of the Ca-form should not be made; not less than 3–5% of the sulpho-groups of the cation-exchange resin should remain in the H-form.

In optimising the conditions for the chromatographic separation of glucose and fructose, it is essential to take into account the fact that an increase of process temperature lead in this instance not only to the acceleration of the mass exchange of the carbohydrates within the cation exchanger beads but also to a shift of the mutarotation equilibrium of the sugars in the liquid phase and to a decrease of the strength of the complexes of the monosaccharides with calcium. A significant increase of the efficiency of the separation of glucose and fructose can be attained by employing cation exchanger beads with the smallest possible size. The latter makes it possible to improve the resolution of the glucose and fructose peaks, to increase the flow rate of the mobile phase, and to increase the amount of charge applied to the column.

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Triplet Exciplexes in the Photochemistry of Quinones

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The results of studies on the kinetics and mechanisms of reactions involving the transfer of an electron and a hydrogen atom to quinone molecules in triplet states are surveyed and the spectroscopic-kinetic characteristics of the triplet exciplexes of quinones and the role of the electron donor-acceptor interactions and hydrogen-bonded complexes in the photochemistry of quinonoid compounds are examined. Attention is concentrated on the experimental investigation of the kinetics and mechanisms of the primary photochemical processes by modern flash photolysis methods.
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INTRODUCTION

Under the influence of light, quinonoid compounds (Q) enter into a wide variety of chemical reactions. In most cases the primary step in the photochemical reactions of quinones is the transfer of an electron and a hydrogen atom to the molecules of quinones in triplet states (^{3}Q), electron donor—acceptor interactions and the formation of a hydrogen bond playing an important role in these processes.

A number of reviews have been devoted to the photochemistry of quinones[1-6] and the photochemical oxidation-reduction reactions of chloroquinones have been examined.[7] This review is devoted to the primary steps in the photochemical reactions of quinones, the transfer of an electron and a hydrogen atom to the molecules of quinones in triplet states, and also the properties of triplet exciplexes.

Important data on the kinetics of the elementary reactions and the mechanism of the transfer of an electron and a hydrogen atom with participation of ^{3}Q have been obtained in recent years, in many respects as a result of the development of methods for the investigation of fast reactions, especially flash photolysis with laser excitation sources in the nanosecond and picosecond ranges; the formation of triplet exciplexes in these chemical processes has been demonstrated.

II. ELECTRON DONOR–ACCEPTOR COMPLEXES OF QUINONES IN THE GROUND AND TRIPLET STATES

1. Electron Donor–Acceptor Complexes of Quinones in the Ground State

Quinonoid compounds are relatively strong electron acceptors and form electron donor–acceptor complexes (EDA complexes) with compounds having electron-donating properties.[8] The energy of the bond between the molecules in the EDA complexes is usually close to that characteristic of the van der Waals interaction and is comparable to or somewhat exceeds kT,[8] the nature of the interaction between the donor and acceptor in the complex being extremely varied.[9]

In the crystalline state and in the absence of a localised interaction, the planes of the rings of the quinone and of the aromatic molecule comprising the EDA complex are parallel and the distance between them is 3.1–3.55 Å.[8] In the presence of a hydrogen bond, the parallel arrangement breaks down; for example, when the donor is phenol, then the angle between the ring planes reaches 10°.[10] The energy of the hydrogen bond in the complex of *p*-benzoquinone (I) with phenol is 5.05 kcal mol^{-1} in the crystalline state, while the entropy is 15 cal mol^{-1} K^{-1}.[11]

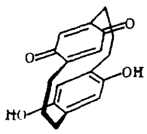
The study of the IR spectra of crystalline complexes of compound (I) with aniline derivatives demonstrated the presence of two non-equivalent carbonyl groups in the molecule of compound (I), which is due to the localised character of the interaction and the appreciable contribution by the ionic component.[2] The formation of complexes between compound (I) and donors having a primary or secondary amino-group is promoted additionally by the presence of a hydrogen bond between the NH and C=O groups to which the ionic component makes an appreciable contribution. The slight non-equivalence of the carbonyl groups in the molecule of compound (I) is also observed in the complex of this compound with *NN*-dimethylaniline and is caused by the localised charge transfer from the unshared pair of the N atom to one of the C=O groups. In the EDA complex of compound (I) with *NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD) the C=O groups are equivalent in the crystalline state; the complex is ionic with a delocalised interaction.

Quinones do not form EDA complexes with triethylamine and bipyridyl in solutions, apparently as a consequence of the steric hindrance generated by the alkyl substituents in the donor. The formation of EDA complexes with amines of the type of triethylenediamine and quinuclidine in solutions has been noted.[13]

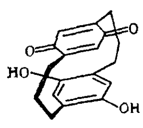
The formation of EDA complexes between quinones and electron donors is accompanied by the appearance in the IR spectrum of a charge-transfer (CT) band.[8] The energy of the CT band is a linear function of the one-electron half-wave potential for the reduction of the quinone in acetonitrile, i.e. $E_{1/2}(Q^-/Q)$, the slope being 0.95 for hexamethylbenzene and 0.8 for other donors.[14] The different slopes of the above relations for hexamethylbenzene compared with other donors may be explained by the steric influence of the methyl groups in the donor, which increases the distance between the donor and the quinone in the EDA complex.[15] The slopes of the analogous relations between the energy of the CT band and the ionisation potential of the aromatic electron donor are close to 0.9.[15,16] A slight deviation from the linear relation between the energy of the CT band and $E_{1/2}(Q^-/Q)$ has been observed for quinones with strong electron-accepting substituents [cyano-derivatives of the quinone (I)].[17]

The occurrence of a localised interaction influences significantly the position of the CT band. This is particularly pronounced for complexes of the quinhydrone type. Thus the formation of a relatively weak hydrogen bond in the EDA complexes of quinones with hydroquinones or *p*-phenylenediamines on passing from a solution to the crystalline state leads to a decrease of the energy of the CT transition by 5000–11000 cm^{-1}.[18–21] This shift is caused precisely by the formation of the hydrogen bond, since the position of the CT band in the spectra of complexes without a hydrogen bond depends only slightly on the state of aggregation.

The pronounced dependence of the interaction in the complexes of the quinhydrone type on the mutual orientation of the quinone and the donor has been demonstrated in a study of the paracyclophane derivatives (A) and (B):[22]



(A)



(B)

The CT band in the spectrum of compound (A) is observed at 462 nm, while the intensity of the absorption of compound (B) in this region is 30 times lower; its CT band has a maximum at 346 nm. The methoxy-derivatives of (A) and (B) behave analogously. Consequently, the hydrogen bonds in these structures do not play any role (the presence of the hydrogen bonds in the crystalline complexes shifts the CT band to the region of 600 nm[19]). The electron donor–acceptor interaction in the given structures is analogous to the interaction in the corresponding π-complexes formed in solution. A CT band has also been observed for multilayer structures analogous to those of compounds (A) and (B) but with an additional benzene ring between the quinone and the hydroquinone; however, the relative orientation of the donor and the acceptor in such structures does not play any role.[23]

The energy of the CT state in the EDA complexes of quinones depends significantly also on the molecular environment. The increase in solvent polarity on passing from cyclohexane to acetonitrile lowers the energy of the CT transition from 1.43 to 1.34 eV for the EDA complex of chloranil (II) with TMPD.[24]

Specific interaction with the medium may exert a strong influence on the formation of quinhydrone complexes in solution. The spectra of the EDA complexes of *ortho*-quinones with the corresponding hydroquinones contain a CT band with the maximum at 440 nm. However, on dissolution of the specimens in alcohols and ethers, the formation of complexes is not observed owing to the presence of hydrogen bonds to solvent molecules.[25]

Quinones are also capable of forming complexes with aromatic amines having an ionic structure.[8,26] The ionic complexes can exist simultaneously with the non-polar EDA complexes and can be detected only in relatively polar solvents or crystals. The dynamics of the system incorporating simultaneously the polar and non-polar EDA complexes has been investigated in detail for complexes of compound (II) with TMPD.[24,27–32] Apart from the absorption characteristic of the non-polar EDA complex, a 3 : 1 mixture of ethyl ether and isopropyl alcohol exhibits bands at 635, 520, and 434 nm due to the absorption by the corresponding radicals and there is an inverse CT band at 1100 nm.[29,30] The formation of radicals in this system has been demonstrated by EPR.[24] The equilibrium

$$Q + D \rightleftarrows Q \ldots D \rightleftarrows Q^- \ldots D^+ \qquad (1)$$

has been postulated.

Ionic complexes arise when the concentration of the non-polar EDA complex exceeds a specific value;[29,30] they are formed on aggregates of non-polar EDA complexes of the cluster type as a result of the increased polarity of the micro-environment in these aggregates, which promotes ionisation. However, the aggregation of neutral EDA complexes has not been observed by Staab and Herz[22] even at temperatures down to 185 K.

In polar solvents neutral EDA complexes of quinones with aromatic amines dissociate into free radical-ions,[8,26,27] whose presence in acetonitrile solutions of compound (II) with TMPD has been detected by EPR.[31] The kinetics of the dissociation reaction have been investigated by flash photolysis in acetonitrile solutions of TMPD and 2.6-diphenyl-1,4-benzoquinone (III);[34] the EDA complexes dissociate with a rate constant of 5.5×10^3 s^{-1} and the enthalpy and entropy of activation are 3.6 kcal mol^{-1} and -29 cal mol^{-1} K^{-1} respectively. The large negative entropy indicates a significant reorganisation of the molecules of the medium on dissociation of the non-polar EDA complex into radical ions. Comparison of the dissociation constants with $E_{1/2}(Q^-/Q)$ for a series of quinones showed that the experimentally observed free energy of electron transfer is below values calculated from the corresponding one-electron potentials.[34]

It is noteworthy that in the quinhydrone complexes thermal electron and hydrogen atom transfer reactions take place.[20,21,25]

Thus the structure of the molecular environment as well as the mutual orientation of the reactants in the complex and the specific features of the interactions between them influence significantly the energy of the state with total charge transfer and hence the kinetics of the reactions involving the charge transfer stage.

2. Triplet Exciplexes of Quinones

The electron affinity of the molecule in an electronically excited state is higher than in the ground state by an amount which is usually set equal to the excitation energy.[35] For this reason, EDA complexes in the triplet state—the triplet exciplexes (TE)—have a structure characterised by a higher contribution of the state with total charge transfer compared with the structure of the corresponding EDA complexes in the ground state. Like the EDA complexes in the ground state, the TE can also be divided on the basis of their structure into polar and non-polar depending on the contribution of the polar state with total CT.

The non-polar triplet states of the EDA complexes of quinones differ significantly in their characteristics from the corresponding ^{3}Q. For example, compound (I) and its derivatives virtually do not phosphoresce in frozen solutions in solvents without electron-donating properties. The introduction of weak electron donors (aromatic hydrocarbons) into these solutions leads to a significant increase of the phosphorescence intensity,[36-38] which is observed on photo-excitation at the wavelength in the region of the CT band. The phosphorescence bands of the EDA complexes of quinones are broadened and displaced to longer wavelengths compared with the phosphorescence spectra of the quinone and to a greater extent the higher the electron-donating capacity of the aromatic hydrocarbon.[38] The phosphorescence spectra of the EDA complexes of compound (I) and its derivatives with aromatic hydrocarbons are similar, as regards the position and form of the bands, to the phosphorescence spectrum of the initial quinone, which shows that the main contribution to the structure of the EDA complexes in the triplet state comes from the structure with excitation localised at the quinone molecule.

The triplet states of the EDA complexes with localised excitation, formed by compound (II) and weak electron donors, have been detected from their absorption by flash[39] and laser[40,41] photolysis methods. The triplet–triplet absorption spectra of solutions of compound (II) in benzene, acetone, and dioxan at room temperature or in a diethyl ether–isopentane–ethyl alcohol (EPA) mixture in the presence of methyl methacrylate at 77 K have weak bands in the range $\lambda > 550$ nm, there is virtually no absorption of compound (II) in the triplet state. The triplet exciplexes formed on quenching of duroquinone (IV) in the triplet state by weak electron donors in non-polar solvents and in acetonitrile have analogous absorption spectra.[42-44]

The photoexcitation of the EDA complexes of quinones in the region of the CT band in systems where the energy of the state with total charge transfer is below that of the triplet state does not lead to the formation of any intermediates.[38,45-48] The main channel leading to the deactivation of the polar electronically excited singlet state of the EDA complex is rapid non-radiative transition to the ground state. The rate of this process is determined by the rate of the vibrational relaxation and the relaxation processes in the molecular environment and amounts to $\geq 10^{11}$ s^{-1}, which is significantly higher than the rate of dissociation into radical-ions and the rate of the singlet–triplet transitions.[49]

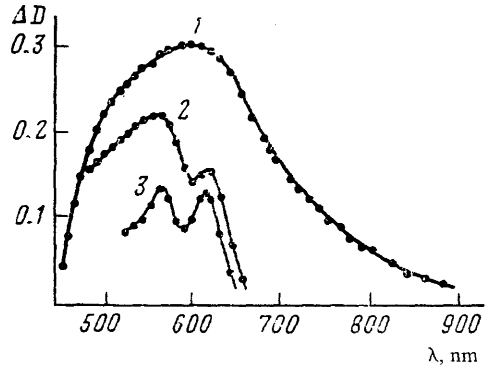


Figure 1. Absorption spectra of solutions of 2,6-diphenyl-1,4-benzoquinone and *NNN'N'*-tetramethyl-1,4-phenylenediamine in dibutyl phthalate (subjected to laser photolysis) obtained at the end of the laser pulse: *1*) ^{3}Q (obtained in the absence of TMPD); *2*) polar TE (obtained at a TMPD concentration of 0.15 M); *3*) absorption spectrum of TMPD radical-cation in acetonitrile.[46]

On quenching ^{3}Q by electron donors in the systems indicated, the formation of polar TE is observed.[43-46] The absorption spectra of the TE contain bands characteristic of the corresponding radical-ions, which is typical for exciplexes with total charge transfer. Absolute agreement between the absorption spectra of the polar TE in inert solvents and the absorption spectra of the corresponding radical-ions is not observed as a consequence of the pronounced overlap of the electron clouds of the radicals in complexes of the "sandwich" type. For example, the absorption spectrum of the polar TE of compound (III) with TMPD contains bands characteristic of the TMPD radical-cation, but the ratio of the intensities of these bands in the spectra of TE and $TMPD^+$ is different (Fig.1). The presence of hydrogen bonds between the radical-ions in the polar TE results in a greater similarity between the absorption spectra of the TE and the radical-ions. For example, the absorption spectrum of the TE of the compound (III)—diphenylamine (DPA) systems shown in Fig.2 is virtually identical with the absorption spectrum of the DPA radical-cation.[45,50] The formation of a hydrogen bond reduces the electron overlap between the radicals as a consequence of the breakdown of the "sandwich" structure. Chemically induced nuclear polarisation (CINP), which arises in the course of photolysis via a triplet mechanism on geminal recombination of the radical-ion pairs, is observed in this system.[50] It has been noted for analogous systems involving compound (II) that the absorption spectrum of the radical-anion components of the hydrogen bonded TE agrees with the absorption spectrum of the radical-anion of compound (II) in alcoholic solutions, where hydrogen bands are formed with solvent molecules.[51,52]

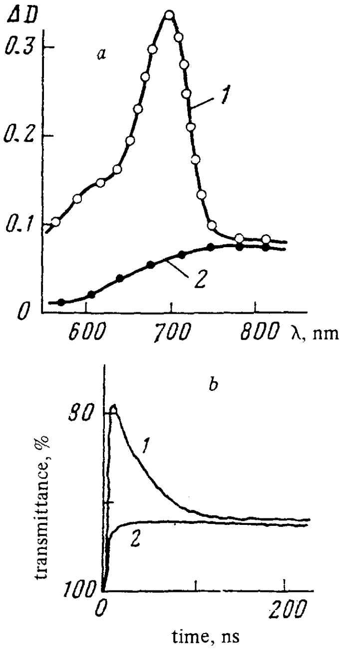


Figure 2. *a*) Absorption spectra of toluene solutions of 2,6-diphenyl-1,4-benzoquinone and Ph_2NH subjected to laser photolysis at −12 °C: *1*) obtained at the end of the laser pulse (superposition of TE and $Ph_2N^\cdot$ spectra); *2*) 150 ns after the laser pulse ($Ph_2N^\cdot$ spectrum); *b*) kinetics of the destruction of TE recorded from the absorption at 690 nm (curve *1*) and of the formation of $Ph_2N^\cdot$ at 830 nm (curve *2*).[50]

The introduction of solvating additives, for example, alcohols, induces a change in the absorption spectra of polar TE. When the methanol content in benzene is 10%, the absorption spectra of the TE virtually correspond to a superposition of the absorption spectra of the corresponding radical-ions.[43,44,53] The alcohol molecules form hydrogen bonds with the quinone radical-anion in the TE.[54] Solvated polar TE have the structure of a solvate-separated ion pair.

In systems characterised by close energies of the state with total CT and a localised excitation, solvation induces the most pronounced changes in the structure of the TE and shifts the equilibrium [a scheme of type (I) with participation of ^3Q] towards the formation of radical-ion pairs in a triplet state.[42–44] For example, the introduction of an insignificant amount of methanol into benzene (the dielectric constant of the solvent hardly changes under these conditions) or an increase of the dielectric constant of the medium to 5 by introducing the corresponding amount of acetonitrile into benzene leads to the formation of radical-ion pairs on photoexcitation of the quinone (IV) in the presence of triphenylamine (TPA) or even at relatively low TPA concentrations, where the formation of a polar TE in this system in benzene is hardly observed.[44] The influence of solvation and of the dielectric constant of the medium is caused by the change in the energy of the state with total CT.

The rate constant for the non-radiative conversion to the ground state (k_{TE}) of polar TE with an energy exceeding 1 eV [for example, the TE of the compound (III)—TPA system] depends only slightly on the polarity and viscosity of the solvent (Table 1). In the case of TE with a low energy, this constant diminishes with increasing polarity of the medium [the TE of the system compound (III)—TMPD (Table 1)]. Solvation by methanol increases or diminishes the k_{TE} of polar TE with high and low energies respectively. The value of k_{TE} increases as the energy of the state with total CT is reduced[43,54] and deviations from this relation are observed only for very low values of the energy indicated.

The kinetics of the non-radiative deactivation of the TE of quinones by transition to the ground state obey the energy gap rule for internal conversion processes, which indicates the important role of the Franck—Condon factor in processes involving the non-radiative deactivation of TE. The same factor is responsible for the increase of k_{TE} on formation of hydrogen bonds with the molecules of the medium or between the radicals in the TE. The constant k_{TE} diminishes slightly when the pressure is raised to 3 kbar.[55]

Triplet exciplexes participate as intermediate species in many photochemical reactions of quinones—photoaddition, photosubstitution, sensitised photoisomerisation, and photodecomposition. Thus p-benzoquinone is photochemically stable in benzene but 4-phenoxyphenol is formed in the presence of difluoroacetic acid.[56] It has been suggested that this reaction includes a stage in which a non-polar TE is formed as a biradical adduct in which acid catalysed proton transfer takes place. The existence of this adduct has been confirmed by the CINP method on photoexcitation of the EDA complex of fluoranil with benzene in the region of the CT band.[57] The TE consisting of a biradical adduct or having a structure with a significant contribution by the state with total charge transfer, also participates in the cycloaddition of olefins to quinones in the triplet state.[58–62] These exciplexes are quenched by O_2, SO_2, and nucleophiles and are protonated in the presence of acids with formation of various products. The simultaneous study by the CINP and picosecond laser photolysis methods of the nature of the intermediates arising in the photolysis of the chloranil—1,1-dimethylindene system in acetonitrile showed that the primary product of the interaction of ^3Q with the olefin is a radical-ion pair.†

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† See P.M.Rentzepis, D.W.Steyert, H.D.Roth, and C.I.Abelt, J.Phys.Chem., 1985, 89, 3955.

Table 1. The rate constants for the destruction of triplet exciplexes of quinones at room temperature.

Electron donor	Solvent	$10^{-6}\,k_{TE}$, s^{-1}	Refs.
Duroquinone			
2-Methoxynaphthalene	Benzene	0.6	[42]
"	Acetonitrile	0.4	[42]
Triphenylamine	Benzene	0.5	[44]
	Benzene–methanol (20:1)	3.0	[44]
2,6-Diphenyl-1,4-Benzoquinone			
Triphenylamine	Benzene	5.0	[53]
"	Toluene	5.1	[53]
"	Perfluorobenzene	5.0	[53]
"	1,4-Dioxan	8.6	[53]
"	Liquid paraffin	5.6	[53]
"	Dibutyl phthalate	7.2	[53]
"	Tetrahydrofuran	7.6	[53]
"	Tetrachloroethane	27	[53]
"	Pentyl alcohol	19	[53]
"	Benzene–methanol (20:1)	12	[53]
Diphenylamine	Toluene	28	[50]
"	Perfluorobenzene	11	[50]
"	Tetrahydrofuran	10	[50]
"	Dibutyl phthalate	68	[50]
"	Liquid paraffin	12	[50]
4-Phenylaniline	Dioxan	50	*
"	Benzene	25	*
"	Toluene	25	*
"	$CHCl_3$	22	*
"	CH_2Cl_2	35	*
"	1,1,2,2-Tetrachloroethane	19	*
"	1,2-Dichloroethane	32	*
"	Tetrahydrofuran	55	*
NN-Dimethyl-4-methoxyaniline	Toluene	23	[84]
NNN'N'-Tetramethyl-*p*-phenylenediamine	Toluene	⩾50	[45]
"	Dibutyl phthalate	26	[45]
"	Tetrahydrofuran	30	[45]
3-Chloro-2,6-diphenyl-1,4-benzoquinone			
Naphthalene	Benzene	9.5	[43]
"	Benzene–methanol (20:1)	11	[43]
1,2,3-Trimethoxybenzene	Benzene	1.6	[43]
"	Benzene–methanol (20:1)	2.7	[43]
4-Phenylaniline	Toluene	42	*
"	1,1,2,2-Tetrachloroethane	51	*
Triphenylamine	Benzene	6.4	[43]
"	Benzene–methanol (20:1)	13	[43]
NN-Dimethyl-4-methoxyaniline	Benzene	12	[43]
"	Benzene–methanol (20:1)	18	[43]
NNN'N'-Tetramethyl-*p*-phenylenediamine	Benzene	⩾50	[43]
3,5-Dichloro-2,6-diphenyl-1,4-benzoquinone			
Triphenylamine	Benzene	10	[43]
"	Benzene–methanol (20:1)	21	[43]
4-Phenylaniline	Toluene	⩾140	*
Chloranil			
Triphenylamine	Benzene	15	[43]
"	Benzene–methanol (20:1)	25	[43]
1-Methylimidazole	Dioxan	6.5	[51]
1-Methylbenzimidazole	Dioxan	5.0	[51]
2-Ethylindazole	Dioxan	⩾50	[51]
Indole	Dioxan	⩾50	[51]
1-Ethylindole	Dioxan	⩾50	[51]
4-Phenylaniline	Toluene	⩾140	*
Diphenylamine	1,2-Dichloroethane	110	[48]
Durene	1,2-Dichloroethane	20	[48]
"	Ethyl acetate	20	[48]
"	Dioxan	17	**
"	Benzene	22	**
"	Ether	40	**
"	Dichloromethane	21	**
"	CCl_4	31	***
Hexamethylbenzene	Benzene	21	***
"	CCl_4	26	***
Pentamethylbenzene	Benzene	20	***
"	CCl_4	23	***
p-Xylene	Benzene	10	***
"	CCl_4	6.2	***
Mesitylene	Benzene	11	***
"	CCl_4	7.6	***
m-Xylene	Benzene	1.8	***
"	CCl_4	2.1	***
Toluene	Benzene	0.52	***
"	CCl_4	0.56	***

It has been suggested that the initial formation of polar TE is a universal process in many photochemical addition reactions involving quinones.[62] The study of the CINP in the photoisomerisation of olefins[63] and various cyclic hydrocarbons,[64-69] in the photodecomposition of thymine dimers,[70] and in the dimerisation of olefins and the dissociation of their cyclic dimers[71] and of the anthracene dimer,[72] all sensitised by quinones, has shown that all these reactions include a step in which radical-ion pairs are formed as a consequence of electron transfer from the reactant to ^3Q. The primary step in the nucleophilic substitution of sulpho-derivatives of 9,10-anthraquinone (V) in the presence of aliphatic amines is electron transfer from the amine to the quinone molecule in the triplet state with subsequent substitution in the radical-ion pair.[73] The photosubstitution of the hydroxy- and amino-derivatives of compound (V) takes place analogously.[74] In the decarboxylation of uric acid sensitised by quinones electron transfer to ^3Q also occurs.[75]

III. ELECTRON TRANSFER TO QUINONE MOLECULES IN TRIPLET STATES

1. Kinetics of the Quenching of Quinone Molecules in Triplet States by Electron Donors

The kinetics and mechanism of the quenching of the triplet states of quinones by electron donors in liquid solutions have been investigated by laser flash photolysis methods. The rate constants for the quenching of the triplet states of compounds (IV),[42,44,76-82] (II),[40,48,51,52,83] and III,[45,46,84] 2-methyl-1,4-naphthoquinone (VI),[85] 2-sulpho-9,10-anthraquinone (VII),[86-88] and anthanthrone (VIII),[89,90] by various electron donors have been obtained (Table 2). The kinetics of the quenching of the triplet state of compound (VIII) by free radicals, which serve as electron donors in this reaction, have also been studied.[91] The rate constants for the quenching of the triplet state of 2,6-disulpho-9,10-anthraquinone (or its solvate) in water by various anions have been estimated as 10^6–10^7 litre mol^{-1} s^{-1}.[92,93] The triplet state of 2-methanesulphonyl-9-10-anthraquinone is quenched by Cl^- in water with a rate constant of ~10^7 litre mol^{-1} s^{-1}.[94]

Table 2. The rate constants for the quenching of the triplet states of quinones by electron and hydrogen atom donors in liquid solutions at room temperature.

Quenching agent	Solvent	k_q, litre $mol^{-1}s^{-1}$	Refs.
Duroquinone			
NN-Dimethyl-4-methoxyaniline	Benzene	$1.2\cdot10^{10}$	[42]
"	Acetonitrile	$1.3\cdot10^{10}$	[42]
"	Methanol	$1.4\cdot10^{10}$	[42]
NN-Dimethylaniline	Benzene	$7.7\cdot10^{9}$	[42]
"	Acetonitrile	$9.9\cdot10^{9}$	[42]
"	Methanol	$1.1\cdot10^{10}$	[42]
NN-Diethylaniline	Cyclohexane	$8.0\cdot10^{9}$	[77]
"	Acetonitrile	$9.4\cdot10^{9}$	[77]
Aniline	Water–methanol (4:1), pH 8	$3.0\cdot10^{9}$	[81]
$PhNH_3^+$	Water–methanol (4:1), pH 2.4	$5.0\cdot10^{7}$	[81]
"	Water–methanol (4:1), pH ~2	$<10^{7}$	[81]
Diphenylamine	Benzene	$7.3\cdot10^{9}$	[42]
"	Acetonitrile	$7.5\cdot10^{9}$	[42]
"	Methanol	$8.4\cdot10^{9}$	[42]
"	Wather–ethanol (2:1)	$3.0\cdot10^{9}$	[78]
Tri-*p*-tolylamine	Benzene	$6.7\cdot10^{9}$	[42]
"	Acetonitrile	$1.0\cdot10^{10}$	[42]
"	Methanol	$1.0\cdot10^{10}$	[42]

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*See P.P.Levin and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 1986, 2587.

**See H.Kobashi, T.Kondo, and M.Funabashi, Bull.Chem. Soc.Japan, 1986, 59, 2347.

***See P.P.Levin and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 1986, 1435.

Table 2 (cont'd)

Quenching agent	Solvent	k_q, litre mol^{-1}s^{-1}	Refs.
	Duroquinone		
Triphenylamine	Benzene	$6.5\cdot10^7$	[42]
"	Acetonitrile	$7.8\cdot10^9$	[42]
"	Methanol	$8.0\cdot10^9$	[42]
Tri-*p*-bromophenylamine	Benzene	$4.2\cdot10^6$	[42]
"	Acetonitrile	$6.4\cdot10^9$	[42]
"	Methanol	$8.0\cdot10^9$	[42]
Trimethylamine	Water–methanol (4:1), pH 11	$3.0\cdot10^9$	[81]
Me_3NH^+	Water–methanol (4:1), pH 7	$<10^7$	[81]
Triethylamine	Cyclohexane	$2.0\cdot10^9$	[77]
"	Acetonitrile	$6.0\cdot10^9$	[77]
Et_3NH^+	Water–methanol (4:1), pH 2	$<10^6$	[81]
Triethylamine	Isopropyl alcohol	$7.1\cdot10^8$	[76]
Et_3NH^+	Water–methanol (4:1), pH −2	$<10^6$	[81]
s-Butylamine	Isopropyl alcohol	$2.3\cdot10^8$	[76]
Diazabicyclooctane	Water–methanol (4:1), pH 2.1	$1.3\cdot10^7$	[81]
"	Water–methanol (4:1), pH 0	$3.0\cdot10^6$	[81]
$CH_3CH(CO_2^-)NH_2$	Water–methanol (4:1), pH 10.2	$1.0\cdot10^5$	[81]
$CH_3CH(CO_2^-)NH_3^+$	Water–methanol (4:1), pH 5.4	$5\cdot10^5$	[81]
$^-O_3SCH_2NH_2$	Water–methanol (4:1), pH 7.2	$2.7\cdot10^7$	[81]
$NCCH_2NH_2+NCCH_2NH_3^+$	Water–methanol (4:1), pH 5.3	$1\cdot10^6$	[81]
$NCCH_2NH_3^+$	Water–methanol (4:1), pH 3.3	$<10^5$	[81]
NH_3	Water–methanol (4:1), pH 10–11	$3.0\cdot10^6$	[81]
NH_4^+	Water–methanol (4:1), pH 4–5	$<10^5$	[81]
1,3,5-Trimethoxybenzene	Water–ethanol (2:1)	$3.3\cdot10^9$	[78]
1,2,3-Trimethoxybenzene	Benzene	$5.5\cdot10^7$	[42]
"	Acetonitrile	$2.2\cdot10^8$	[42]
"	Methanol	$3.0\cdot10^9$	[42]
2-Methoxynaphthalene	Benzene	$4.2\cdot10^7$	[42]
"	Acetonitrile	$1.0\cdot10^8$	[42]
"	Methanol	$2.2\cdot10^9$	[42]
Dibenzo-18-crown-6 ether	Benzene	$7.6\cdot10^6$	[42]
"	Acetonitrile	$5.5\cdot10^7$	[42]
"	Methanol	$9.5\cdot10^8$	[42]
2,3-Dimethylnaphthalene	Benzene	$3.2\cdot10^6$	[42]
"	Acetonitrile	$3.3\cdot10^8$	[42]
"	Methanol	$4.3\cdot10^7$	[42]
2,6-Dimethylnaphthalene	Benzene	$1.6\cdot10^8$	[42]
"	Acetonitrile	$3.3\cdot10^6$	[42]
"	Methanol	$1.1\cdot10^8$	[42]
Pentamethylbenzene, naphthalene	Benzene, acetonitrile, methanol	$<5\cdot10^4$	[42]
Cl^-	Water–methanol (4:1), pH 7	$1.0\cdot10^7$	[81]
"	Water–methanol (4:1), pH −2	$1.0\cdot10^9$	[81]
Br^-	Water–methanol (4:1), pH 7	$4.0\cdot10^9$	[81]
OH^-	Water–methanol (4:1), pH 10–12	$1.5\cdot10^9$	[81]
I^-	Water–methanol (4:1), pH 7	$9.0\cdot10^9$	[81]
"	Acetonitrile	$9.9\cdot10^9$	[82]
Ag^+	Water–methanol (2.3:1)	$1.5\cdot10^6$	[82]
"	Acetonitrile	$5\cdot10^5$	[82]
Fe^{2+}	Water–ethanol (2:1)	$1.3\cdot10^9$	[78]
$Fe(CN)_6^{4-}$	Water–ethanol (2:1)	$2.6\cdot10^9$	[78]
"	Water–methanol (2.3:1)	$4.3\cdot10^9$	[82]
$IrCl_6^{3-}$	Water–methanol (2.3:1)	$4.1\cdot10^9$	[82]
SCN^-	Water–methanol (2.3:1)	$4.6\cdot10^9$	[82]
"	Acetonitrile	$8.1\cdot10^9$	[82]
CO_3^{2-}	Water–ethanol (2:1)	$7.3\cdot10^7$	[78]
Durohydroquinone	Isopropyl alcohol	$2.1\cdot10^9$	[150]
"	Cyclohexane	$6.2\cdot10^9$	[149]
"	Ethanol	$3.9\cdot10^9$	[149]
4-Phenylphenol	Benzene	$1.2\cdot10^{10}$	[42]
"	Acetonitrile	$2.3\cdot10^9$	[42]
"	Methanol	$6.9\cdot10^9$	[42]
	Chloranil		
Naphthalene	Propionitrile	$7.0\cdot10^9$	[83]
Acrylonitrile	1,2-Dichloroethane	$3.1\cdot10^4$	[40]
Durene	1,2-Dichloroethane	$3.1\cdot10^9$	[48]
Methyl methacrylate	1,2-Dichloroethane	$5.1\cdot10^6$	[40]
"	Acetonitrile	$6.7\cdot10^8$	[40]
Styrene	1,2-Dichloroethane	$2.5\cdot10^9$	[40]
"	Acetonitrile	$8.0\cdot10^9$	[40]
Pyrazole	Dioxan	$4\cdot10^7$	[51]
"	Acetonitrile	$7\cdot10^7$	[51]
Imidazole	Dioxan	$2.0\cdot10^9$	[51]
"	Acetonitrile	$4.1\cdot10^9$	[51]
1-Methylimidazole	Dioxan	$2.6\cdot10^9$	[51]
"	Acetonitrile	$4.7\cdot10^9$	[51]
Benzimidazole	Dioxan	$1.4\cdot10^9$	[51]
"	Acetonitrile	$6.3\cdot10^9$	[51]

Table 2 (cont'd)

Quenching agent	Solvent	k_q, litre mol^{-1}s^{-1}	Refs.
	Chloranil		
1-Methylbenzimidazole	Dioxan	$1.1\cdot10^9$	[51]
"	Acetonitrile	$4.8\cdot10^9$	[51]
Indazole	Dioxan	$1.4\cdot10^9$	[51]
"	Acetonitrile	$5.3\cdot10^9$	[51]
2-Ethylindazole	Dioxan	$3.4\cdot10^9$	[51]
"	Acetonitrile	$9.6\cdot10^9$	[51]
Indole	Dioxan	$5.0\cdot10^9$	[51]
"	Acetonitrile	$1.3\cdot10^{10}$	[51]
1-Ethylindole	Dioxan	$5.4\cdot10^9$	[51]
"	Acetonitrile	$1.2\cdot10^{10}$	[51]
Tetrachlorohydroquinone	Dioxan	$1.7\cdot10^9$	[152]
"	1,2-Dichloroethane	$3.6\cdot10^9$	[152]
"	Acetonitrile	$4.7\cdot10^9$	[152]
	Fluoranil		
Tetrafluorohydroquinone	Benzene	$2.0\cdot10^9$	[57]
	2,6-Diphenyl-1,4-benzoquinone		
NNN'N'-Tetramethyl-*p*-phenylenediamine	Toluene	$1.8\cdot10^{10}$	[45]
	Dibutyl phthalate	$1.1\cdot10^9$	[45]
Triphenylamine	Toluene	$5.0\cdot10^9$	[45]
"	Dibutyl phthalate	$3.3\cdot10^8$	[45]
Diphenylamine	Toluene	$7.9\cdot10^9$	[45]
"	Dibutyl phthalate	$5.1\cdot10^8$	[45]
2,3,5-Trimethylphenol	Benzene	$1.1\cdot10^{10}$	[151]
2,4,6-Trimethylphenol	Benzene	$9.9\cdot10^9$	[151]
4-Phenylphenol	Benzene	$1.0\cdot10^{10}$	[151]
2,6-Diphenylhydroquinone	Benzene	$1.0\cdot10^{10}$	[151]
2,6-Diphenyl-4-diphenylmethylphenol	Benzene	$9.2\cdot10^9$	[151]
6-t-Butyl-2-phenyl-4-diphenylmethylphenol	Benzene	$5.6\cdot10^9$	[151]
2,6-Di-t-butyl-4-diphenylmethylphenol	Benzene	$3.4\cdot10^9$	[151]
2,4,6-Tri-t-butylphenol	Benzene	$2.3\cdot10^9$	[151]
2,3-Dichlorophenol	Benzene	$9.1\cdot10^9$	[151]
3-Nitrophenol	Benzene	$1.3\cdot10^{10}$	[151]
2,6-Di-t-butyl-4-nitrophenol	Benzene	$6.6\cdot10^9$	[151]
4-Nitrophenol	Benzene	$2.7\cdot10^9$	[151]
2,4-Dinitrophenol	Benzene	$4.2\cdot10^9$	[151]
2,6-Dinitrophenol	Benzene	$7.3\cdot10^9$	[151]
2,4,6-Trinitrophenol	Benzene	$9.7\cdot10^9$	[151]
	2-Methyl-1,4-naphthoquinone		
Thymine	Water	$2.7\cdot10^9$	[85]
Uracil	Water	$3.0\cdot10^9$	[85]
6-Methyluracil	Water	$3.2\cdot10^9$	[85]
	2-Sulpho-9,10-anthraquinone		
$NCSe^-$	Water	$3.7\cdot10^9$	[86]
NO_2^-	Water	$3.2\cdot10^9$	[86]
I^-	Water	$4.2\cdot10^9$	[86]
N_3^-	Water	$3.1\cdot10^9$	[86]
Br^-	Water	$3.8\cdot10^9$	[86]
NCS^-	Water	$3.9\cdot10^9$	[86]
OH^-	Water	$0.3\cdot10^9$	[86]
Cl^-	Water	$0.5\cdot10^9$	[86]
ClO_4^-, SO_4^{2-}	Water	$<10^6$	[86]
	Anthanthrone		
NN-Dimethyl-4-methoxyaniline	Benzene	$7.6\cdot10^9$	[89]
"	Acetonitrile	$9.2\cdot10^9$	[89]
Triphenylamine	Benzene	$4.6\cdot10^5$	[89]
"	Acetonitrile	$2.3\cdot10^9$	[89]
4-Aminobiphenyl	Benzene	$4.6\cdot10^9$	[89]
"	Acetonitrile	$5.3\cdot10^9$	[89]
4-Bromoaniline	Benzene	$4.8\cdot10^8$	[89]
"	Acetonitrile	$4.8\cdot10^9$	[89]
4-Methoxybiphenyl	Benzene	$3.5\cdot10^5$	[89]
"	Acetonitrile	$3.9\cdot10^5$	[89]
2,6-Diphenylhydroquinone	Benzene	$2.8\cdot10^9$	[151]
"	Acetonitrile	$2.1\cdot10^9$	[151]
2,4,6-Trimethylphenol	Benzene	$3.2\cdot10^9$	[151]
"	Acetonitrile	$5.8\cdot10^8$	[151]
2,6-Di-t-butyl-4-methylphenol	Benzene	$9.2\cdot10^7$	[151]
"	Acetonitrile	$2.2\cdot10^7$	[151]
2,3,5-Trimethylphenol	Benzene	$2.3\cdot10^9$	[151]
"	Acetonitrile	$4.8\cdot10^8$	[151]
4-Phenylphenol	Benzene	$2.3\cdot10^9$	[151]
"	Acetonitrile	$2.8\cdot10^7$	[151]
2,3-Dichlorophenol	Benzene	$5.3\cdot10^7$	[151]
"	Acetonitrile	$8.3\cdot10^5$	[151]
3-Nitrophenol	Benzene	$1.1\cdot10^7$	[151]
"	Acetonitrile	$1.9\cdot10^6$	[151]
2,6-Di-t-butyl-4-nitrophenol	Benzene	$7.2\cdot10^6$	[151]
"	Acetonitrile	$3.4\cdot10^6$	[151]
4-Nitrophenol	Benzene	$5.7\cdot10^6$	[151]
"	Acetonitrile	$1.0\cdot10^6$	[151]
2,6-Dinitrophenol	Benzene	$4.0\cdot10^5$	[151]
"	Acetonitrile	$8.1\cdot10^5$	[151]
2,4-Dinitrophenol	Benzene	$1.9\cdot10^5$	[151]
"	Acetonitrile	$2.7\cdot10^5$	[151]
2,4,6-Trinitrophenol	Benzene	$5.2\cdot10^4$	[151]
"	Acetonitrile	$1.5\cdot10^5$	[151]

The quenching of excited states by electron transfer is described by the scheme[95,96]

$$^3\mathrm{Q}+\mathrm{D}\underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}}(^3\mathrm{Q}\cdots\mathrm{D})\underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}}{}^3(\mathrm{Q}^-\cdots\mathrm{D}^+)-\left|\begin{array}{l}\xrightarrow{k_{30}}\mathrm{Q}^-+\mathrm{D}^+,\\ \xrightarrow{k_{31}}\mathrm{Q}+\mathrm{D}.\end{array}\right. \qquad (2)$$

Subject to the condition $k_{31} \ll k_{30}$, which is usually fulfilled in polar solvents, the quenching rate constants k_q can be calculated within the framework of this scheme from the formula

$$k_q=\frac{k_{12}}{1+(1/K_{23}+k_{30}/k_{23})\,k_{21}/k_{30}}. \qquad (3)$$

The rate constants for the elementary steps of reaction (2) are calculated from the formulae

$$k_{23}=k^0\exp(-\Delta G^*_{23}/RT), \qquad (4)$$

$$k_{23}/k_{32}=K_{23}=\exp(-\Delta G_{23}/RT), \qquad (5)$$

where k^0 is the frequency factor and ΔG^*_{23} and ΔG_{23} are the free energy of activation and the standard free energy of electron transfer. It is assumed in the above model[95,96] that $k^0 = k_{30}$ and that k_q in acetonitrile can be calculated from the formula

$$k_q,\ \text{litre mol s}^{-1}=2\cdot 10^{10}\{1+0.25\,[\exp(\Delta G^*_{23}/RT)+\exp(\Delta G_{23}/RT)]\}^{-1}, \qquad (6)$$

ΔG^*_{23} is then related to ΔG_{23} by the equation

$$\Delta G^*_{23}=\frac{1}{2}\Delta G_{23}+\left[\left(\frac{1}{2}\Delta G_{23}\right)^2+(\Delta G_{23}(0))^2\right]^{1/2}, \qquad (7)$$

where $\Delta G_{23}(0)$ is the internal barrier to the electron transfer process, amounting to 2.4 kcal mol^{-1} in acetonitrile. Other relations between ΔG^*_{23} and ΔG_{23} have also been proposed—within the framework of parabolic energy surfaces:[97,98]

$$\Delta G^*_{23}=\Delta G_{23}(0)\,[1+0.25\Delta G_{23}/\Delta G_{23}(0)]^2, \qquad (8)$$

and a formula analogous to the corresponding expression for the energy transfer process:[99]

$$\Delta G^*_{23}=\Delta G_{23}+\Delta G_{23}(0)\ln\{1+\exp[-\Delta G_{23}\ln 2/\Delta G_{23}(0)]\}(\ln 2)^{-1}. \qquad (9)$$

ΔG_{23} can be calculated from the oxidation-reduction potentials and the energy of the triplet state.[95,96,100]

The relations between k_q and ΔG_{23}, calculated by Eqn.(6) using Eqns.(7)–(9), are presented in Fig.3, which also includes experimental data on the quenching of the triplet states of compounds (IV) and (VII) by inorganic ions in water as well as compound (IV) in the triplet state in acetonitrile and benzene by aromatic electron donors (Table 2). The relations corresponding to Eqns.(7) and (9) describe satisfactorily the experimental results in a polar medium. The relation corresponding to Eqn.(8) predicts a decrease of k_q for high negative values of ΔG_{23}, which has not been observed experimentally. The causes of the discrepancy between the theory and experiment (the presence of other reaction channels, the characteristic features of the organisation of the medium around the pair of charged and neutral reactants, and the forms of the energy surface) have been discussed.[101,102]

The satisfactory correlation between k_q and ΔG_{23} is not by itself proof that total charge transfer takes place in the course of the quenching process. Thus, whereas in the quenching of compound (IV) in the triplet state by certain inorganic ions and aromatic donors in hydroxylated solvents yields radical-ions even for low values of k_q,[42,78,80] in acetonitrile radical-ions are formed only for values of k_q close to the diffusional limit.[42] In quenching with low constants k_q, the reaction can be achieved via the formation of a non-polar TE, which dissociates slowly into radical-ions. The protonation of ^{3}Q leads to an increase of the electron-accepting capacity. In the protonation of compound (IV) in the triplet state, k_q for the anions increases and that for the cation diminishes (Table 2).[81]

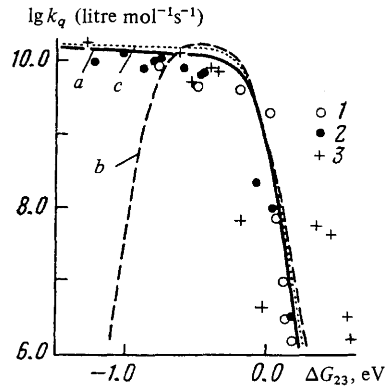

Figure 3. Dependence of lg k_q on ΔG_{23} calculated by Eqn.(6) using Eqns.(7) (*a*), (8) (*b*), and (9) (*c*) and experimental values of k_q obtained in the quenching of quinone molecules in the triplet state by electron donors in different solvents: *1*) water; *2*) acetonitrile; *3*) benzene.

If the intermediate TE is non-polar in both polar and non-polar solvents, then k_q does not change on passing from benzene to acetonitrile (Table 2). Such TE have low dipole moments and their energy depends only slightly on the dielectric constant of the medium ε. The change in the nature of the TE (a transition from non-polar to polar nature) if ε increases entails a sharp break in the relations between k_q and ε, as has been observed in the quenching of certain ^{3}Q by triphenylamine.[44,89] The introduction of solvating additives, which form complexes with TE, is also accompanied by an appreciable increase in k_q (Table 2) as a consequence of the change in the nature and energy of the TE.[42,44,89]

Thus the kinetics and mechanism of the quenching of the triplet states of quinones by electron donors are determined by the properties of the intermediate TE, which are also responsible for the characteristics of the formation reaction of radical-ions in polar media.

2. The Formation of Radical-Ions in Reactions of Quinones in Triplet States

Electron transfer to a quinone molecule in the triplet state in polar media is accompanied by the formation of the quinone radical-anion and the oxidised form of the electron donor, which is frequently the solvent molecule. The radical-ions have been detected by flash and laser photolysis methods in the quenching of the triplet states of compound (IV) by aromatic amines,[34,42,44,54,77–79,82,103,104] aromatic hydrocarbons,[42,78,80] acetone,[78] and inorganic anions;[78,79,81] the triplet state of compound (II) by aromatic amines,[34,48,54,105] heterocyclic compounds,[51,52] aromatic hydrocarbons,[41,42,83,106–108] cyclic hydrocarbons,[64] methyl methacrylate,[40] and certain polar solvents;[39,83,105,108–110] the triplet states of other derivatives of compound (I) by aromatic amines and hydrocarbons;[33,34,45,46,53–55] the triplet state of 1,4-naphthoquinone (IX) by triphenylamine;[54] the triplet state of compound (VI) by pyrimidines,[85] the triplet state of compound (V) and its derivatives by amines[54,111] and inorganic anions;[86,87,92,93,112] the triplet state of compound (VIII) by aromatic amines,[89] and the triplet states of diphenoquinone derivatives by triphenylamine.[54] The formation of radical-ions follows unambiguously from CINP data on the photolysis of compound (II) in polar solvents in the presence of olefins[63,71] and certain cyclic hydrocarbons.[65–69] The formation of radical-ion pairs in the photolysis of t-butyl-substituted derivatives of compound (I) and o-benzoquinone in frozen diethylamine and triethylamine has been observed by EPR,[113,114] but in another study[115] it was concluded that a pair of neutral radicals is formed.

On the basis of chemically induced electron polarisation (CIEP) and CINP data, it has been suggested that the main process in the quenching of ^3Q by aliphatic amines in alcohols is the formation of quinone radical-anions.[116,117] The radical-anion can be formed in the course of secondary proton transfer processes.[118] Thus the formation of quinone radical-anions has been detected by the CIEP method in the photolysis of alcoholic solutions of quinones in the presence of aliphatic amines,[76,119–122] but it has been noted in experimental laser photolysis that the formation reaction of these radicals is slower than the destruction of the initial triplet state.[76] In experiments on picosecond laser photolysis, it was possible to demonstrate unambiguously that the quenching of the triplet state of compound (V) and its chlorinated derivatives by triethylamine in alcohol entails electron transfer.[111] The conclusion, reached on the basis of EPR and CIEP data, that radical-ions are formed in the course of the primary step, in quinone–organometallic donors[118,123–127] and vitamin K_1–vitamin C[128] systems also appears to be fairly unambiguous. In the 9,10-phenanthrenequinone (X)–$Me_3SnSnMe_3$ system, radicals are formed on photoexcitation of the EDA complexes in the region of the CT band.[118] An EPR signal, which was assigned to a radical-ion pair, has been detected in the photolysis of crystalline specimens of 3,6-di-t-butylcatechol with added 3,6-di-t-butyl-1,2-benzoquinone.[129–130]

The formation of radical-ions on interaction of quinones in triplet states with electron donors in polar media usually takes place with yields close to 1.0 in systems where ΔG_{23} is negative and k_q is close to the diffusional limit.[42,78,83] Donors having a radical fragment are an exception, since in this case an ion pair in a doublet spin state is formed. In this state (in contrast to the triplet state) there is no prohibition of the transition to the ground (also doublet) state of the initial reactant.[91] In systems with positive ΔG_{23} and k_q below the diffusional limit, high yields of radicals were observed only in hydroxylated solvents.[42]

Radical-ions are formed in high yields on quenching of ^3Q by electron donors in micellar solutions and microemulsions, where the reactants can be present in both the same and in different phases.[78,79,80,103,104,131] In the latter case electrons are transferred from the surface of the micelle (the site where the donor is located) through the interface to the quinone molecule in the triplet state located within the micelle. This process is very rapid, for example occurring in 40 ns between the molecule of compound (IV) in an anionic micelle and Fe^{2+} [78] and even faster between the same molecule in a cationic micelle and CO_3^{2-},[79] which is due to the operation of a tunnel mechanism. The radicals are not formed in micelles containing Cl^- and Br^- anions owing to the quenching of the triplet state by the latter. This effect is not quite so pronounced in microemulsions, where the molecule in the triplet state is present in the benzene phase and is separated from the ions of the surfactant.[103]

In many cases the quenching of ^3Q by inorganic anions (for example, NO_2^-, CO_3^{2-}, and SO_3^{2-}) is accompanied by the formation of radicals with a high yield.[86,87,92,93,112,132] However, radicals are not formed on interaction with N_3^-, NCS^-, Cl^-, Br^-, and I^-.[81,86,87,92,94] The contribution of quenching due to the heavy atom effect is insignificant, since Cs^+ ions do not quench effectively the triplet state of compound (IV).[81] The dependence of the yield of radicals on the nature of the inorganic anion can be accounted for in terms of the extent of the spin–orbital coupling in the inorganic radical. If the multiplet splitting of the energy levels of the radical, determined by the orbital momentum, exceeds 100 cm^{-1} then the intersystem crossing in the radical pair is accelerated so much that this process becomes the main channel leading to the destruction of the triplet radical pair.[87] The quenching by the NO_2^- anion, which has a triplet state with an energy of 56 kcal mol^{-1}, should be specially mentioned. The quenching by this anion leads to the formation of radicals, i.e. in the presence of two possible reaction channels (energy transfer and electron transfer), both of which are exothermic, the process proceeds via the pathway most favoured by energy factors. It is quite likely that electron transfer is preceded in this instance by energy transfer.

A low quantum yield in the formation of radicals is characteristic also of the quenching by the OH^- anion [in the compound (IV)—OH^- system, the yield of radicals is 10%[77]] as a consequence of the existence of rapid chemical channels leading to the destruction of TE (hydroxylation).[86] Exactly the same adduct formation reaction, competing with dissociation into radical-ions, is responsible for the low efficiency of the formation of radicals on quenching of the triplet state of compound (II) by vinyl monomers.[40]

Low yields of radical-ions have been recorded in the photolysis of quinones in polar solvents without hydroxy-groups [thus the quantum yield is 0.08 in the photolysis of compound (II) in acetonitrile and is smaller by a factor of 3 in propyl cyanide,[40,83] while in the photolysis of compound (IV) in acetone it amounted to 0.08[78]], which is due to the low value of the electron transfer rate constant. The low (0.15) yield of radical-anions in the photolysis of compound (IV) in micellar solutions of sodium lauryl sulphate (the sulphate group is the electron donor) can be explained analogously.[78]

Detailed studies by flash photolysis with measurement of the absorption and electrical conductivity in binary mixtures and viscous alcohols at different pressures have shown that, in the quenching of the triplet states of quinones by aromatic electron donors in media of moderate polarity, radicals are formed as a result of the dissociation of the TE in accordance with the scheme[34,53–55]

$$3Q + D \rightleftarrows TE - \left[\begin{array}{l} \xrightarrow{k_2} Q^- + D^+, \\ \xrightarrow{k_1} Q + D. \end{array}\right. \qquad (10)$$

The rate constant for the dissociation of polar TE into radical-ions (k_2) depends on the viscosity of the medium and can be calculated satisfactorily from the formula for the rate constant for the diffusion-controlled dissociation of ion pairs:

$$k_{dis} = 3e^2D\{\sigma^3\varepsilon kT\,[\exp(e^2/\sigma\varepsilon kT) - 1]\}^{-1}, \qquad (11)$$

where e is the electronic charge, D the mutual diffusion coefficient, and σ the average distance between the ions in the pair.

The values of σ (Table 3), obtained from the dependence of k_{TE} or the yield of radicals on the dielectric constants ε of the binary mixtures (Fig. 4) in most cases significantly exceed the sum of the van der Waals radii of the reactants and also the distance between the unpaired electrons in the analogous radicals pairs in frozen solutions (amounting to 6.0–6.5 Å[38,113]), where the reaction proceeds via EDA or hydrogen-bonded complexes). The presence of a hydrogen bond between the radicals, for example, in the 3-chloro-2,6-diphenyl-1,4-benzoquinone–DPA system, is accompanied by a decrease of σ which is more pronounced the stronger the hydrogen bond. High values of σ reflect the fact that the radicals are formed from solvate-separated radical-ion pairs.

Table 3. The distances (σ/Å) between the radical-ions in triplet exciplexes.*

Quinone	Donor	Solvent		Refs.
		benzene–methanol	benzene–benzonitrile	
9,10-Anthraquinone	Triphenylamine	16.7	—	[54]
1,4-Naphthoquinone	"	17.3	—	[54]
Duroquinone	"	19.2	11.9 (19.7)	[54]
2,6-Diphenyl-1,4-benzoquinone	"	16.0	11.4	[54]
1,4-Benzoquinone	"	15.3	—	[54]
3,5-Dichloro-2,6-diphenyl-1,4-benzoquinone	"	14.2	—	[54]
Chloranil	"	13.4	10.5	[54]
Bromanil	"	12.9	10.9	[54]
4,4′-Diphenoquinone	"	17.0	—	[54]
3,3′,5,5′-Tetrachloro-4,4′-diphenoquinone	"	15.1	11.6	[54]
3,6-Di-t-butyl-1,2-benzoquinone	"	13.6	—	[54]
3-Chloro-2,6-diphenyl-1,4-benzoquinone	"	14.7	—	[54]
"	Naphthalene	15.3	—	[54]
	1,2,3-Trimethoxybenzene	15.6	—	[54]
"		13.8	—	[54]
3-Chloro-2,6-diphenyl-1,4-benzoquinone	*NN*-Dimethylaniline	14.6	—	[54]
"	*NN*-Dimethyl-4-methoxyaniline	15.7	—	[54]
"	*NNN′N′*-Tetramethylbenzidine	15.0	—	[54]
"	*NNN′N′*-Tetramethyl-*p*-phenylenediamine	—	7.5	[34]
3,5-Dichloro-2,6-diphenyl-1,4-benzoquinone	Diphenylamine	—	8.5	[34]
Chloranil	"	—	10.5	[34]
Bromanil	"	—	11.5	[34]

*The value for the benzene–benzonitrile mixture + 5 vol.% methanol is given in brackets.

In the absence of specific interactions of the radicals with one another or with the molecules of the medium, the values of σ are almost independent of the structure of the quinone and the donor (Table 3), but the introduction of alcohols into the system induces an increase of σ which is greater the stronger the hydrogen bond between the radical-anion of the quinone and the alcohol molecule.

The study of the dynamics of the processes in the radical-ion pair in the picosecond time range in electron transfer from aromatic donors to a molecule of compound (II) in the triplet state in acetonitrile showed that the electron transfer is accompanied by the establishment of equilibrium in the cation–anion–molecular environment system over a period of approximately 0.1–0.5 ns.[106] It has been suggested that this thermodynamic equilibrium is attained due to diffusional processes. In the analysis of the spectral changes in the course of the establishment of equilibrium, it was concluded that the distance over which the electron is transferred is less than the equilibrium distance between the radicals in the pair. Analogous experiments in the compound (V)—triethylamine system in alcohol and acetonitrile also indicate the primary formation of a contact radical-ion pair.[111]# However, studies on the benzophenone–amine system have led the authors[133,134] to the conclusion that the radicals formed after electron transfer come closer together.

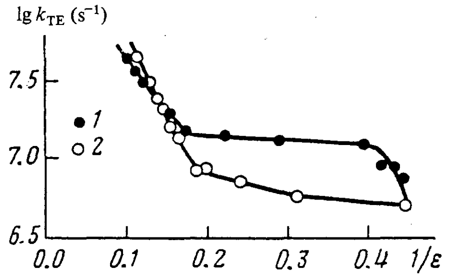

Figure 4. Dependence of lg k_{TE} on 1/ε for the solvent obtained by laser photolysis of solutions of 2,6-diphenyl-1,4-benzoquinone in the presence of triphenylamine in binary benzene–methanol (1) and benzene–benzonitrile (2) mixtures.[53]

IV. HYDROGEN ATOM TRANSFER TO QUINONE MOLECULES IN TRIPLET STATES

The reaction involving the transfer of a hydrogen atom to the molecules of quinones in triplet states can be achieved via three mechanisms. In the two extreme cases their reaction takes place in two stages where an electron is transferred initially followed by a proton [Scheme (12)] or conversely [Scheme (13)]:

$$
\begin{array}{rl}
{}^3Q + RH \rightleftarrows ({}^3Q\cdots RH) \rightleftarrows {}^3(Q^-\cdots RH^+) - & \left[\begin{array}{l}\longrightarrow Q^- + RH^+,\\ \longrightarrow Q + RH,\end{array}\right.\\
\uparrow\downarrow & \\
{}^3(QH^\cdot\cdots R^\cdot) - & \left[\begin{array}{l}\longrightarrow QH^\cdot + R,\\ \longrightarrow Q + RH.\end{array}\right.
\end{array}
\qquad (12)
$$

$$
{}^3Q + RH \rightleftarrows {}^3(Q\cdots RH) \rightleftarrows {}^3(QH^+ \overset{\overset{Q+RH}{\uparrow}}{\cdots} R^-) \rightleftarrows {}^3(QH\cdots R^\cdot) - \left[\begin{array}{l}\longrightarrow QH^\cdot + R^\cdot,\\ \longrightarrow Q + RH.\end{array}\right.
\qquad (13)
$$

In the intermediate case the hydrogen atom is transferred more or less as a single whole:

$$
{}^3Q + RH \rightleftarrows ({}^3Q\cdots RH) \rightleftarrows {}^3(QH^\cdot\cdots R^\cdot) - \left[\begin{array}{l}\longrightarrow QH^\cdot + R^\cdot,\\ \longrightarrow Q + RH.\end{array}\right.
\qquad (14)
$$

Generally speaking the processes enumerated may compete with one another, but the situation where the reaction cannot be assigned to any one of three types is more probable since the intermediate CT stage is described by a superposition of states of different nature and the hydrogen-bonded complex can be characterised by a potential surface with a single minimum for the position of the proton.

#See K.Hamanoue, T.Nakayama, K.Sugiura, H.Teranishi, M.Washio, S.Tagawa, and Y.Tabatu, Chem.Phys.Letters, 1985, 118, 503, and K.Hamanoue, M.Kimoto, Y.Kajiwara, T.Nakayama, and H.Teranishi, J.Photochem., 1985, 31, 143.

The transfer of a hydrogen atom to carbonyl compounds in triplet $n\pi^*$ states has much in common with the analogous process involving alkoxy-radicals and has been considered theoretically as a reaction within the framework of valence bond methods,[135] correlation diagrams,[136] and perturbation theory.[137,138] Furthermore, Formosinho[139,140] carried out calculations for the transfer of a hydrogen atom to carbonyl compounds in triplet states, including quinones, as a tunnel process within the framework of the theory of non-radiative transitions; this approach makes it possible to calculate satisfactorily the rate constants for the transfer of a hydrogen atom in systems with electron donor–acceptor interactions.

1. The Transfer of a Hydrogen Atom in the Interaction of Quinones in Triplet States with Amines

The interaction of quinones in triplet states with secondary and primary aromatic amines in liquid solutions is accompanied by the formation of both radical-ions and neutral radicals as a consequence of electron and hydrogen atom transfer respectively.[34,42,45,50,141] An increase in the temperature of the solution leads to an increased yield of neutral radicals, while the overall yield of radicals does not change. The quenching process takes place with a diffusional rate constant (Table 2); deuteriation of the amino-groups does not cause an appreciable change in the ratio of the yields of radicals of different nature.

Table 4. The equilibrium constant K_H, the enthalpy ΔH_H, and the entropy ΔS_H of the prototropic equilibrium in radical pairs in toluene and acetonitrile.[141]

Quinone	Amine	K_H		ΔH_H, kcal mol^{-1}		ΔS_H, cal mol^{-1} K^{-1}	
		toluene	CH_3CN	toluene	CH_3CN	toluene	CH_3CN
Duroquinone	Diphenylamine	50	2.7	—	5.0	—	19
2,6-Dimethoxy-1,4-benzoquinone	"	34	3.1	8.0	4.8	34	19
2,6-Diphenyl-1,4-benzoquinone	"	25	1.8	9.4	4.5	39	16
3-Chloro-2,6-diphenyl-1,4-benzoquinone	"	8.1	1.0	10.0	4.3	38	15
3,5-Dichloro-2,6-diphenyl-1,4-benzoquinone	"	1.2	0.25	10.4	3.8	36	10
2,5-Dichloro-1,4-benzoquinone	"	0.52	0,17	10.6	3.5	35	9
Chloranil	"	0,04	0.08	11.4	3,3	32	6
3-Chloro-2,6-diphenyl-1,4-benzoquinone	4-t-Butyldiphenylamine	2,8	0.62	9.9	2.7	36	8
"	4,4′-Di-t-butyldiphenylamine	1.4	0.37	10.1	1.6	35	3
"	4,4′-Bis(1,1,3,3-tetramethylbutyl)diphenylamine	1.1	0.28	10.2	1.0	35	1
3,5-Dichloro-2,6-diphenyl-1,4-benzoquinone	4,4′-Di-t-butyldiphenylamine	0.25	0.16	10.8	0.5	34	−2

The above features are characteristic of reactions proceeding via scheme (12). ΔG_{23} is negative and electron transfer is therefore the fastest of the possible reactions. Next, prototropic equilibrium is established in the radical pair and the process also takes place very rapidly in the course of thermodynamic relaxation as a consequence of the presence of a hydrogen bond. Table 4 presents the thermodynamic parameters for the prototropic equilibrium in the radical pairs formed on quenching of the triplet states of quinones by secondary aromatic amines. The reorganisation of the molecules of the medium in the vicinity of the ion pair, which has a significantly higher dipole moment than the pair of neutral radicals, leads to an extremely high ΔS_H. The weakening of the electrostatic field with increase of solvent polarity is accompanied by a decrease of ΔS_H and ΔH_H. The equilibrium shifts towards the ion pair with increase of the acidity of the semiquinone and the basicity of the aminyl radical. A linear relation is observed between the free energy of proton transfer in toluene and acetonitrile, on the one hand, and the free energy of the acid–base equilibrium in water, calculated from the corresponding pK,[141] on the other. U-shaped relations between K_H and ε for the binary toluene–acetonitrile mixture have been obtained, which can be accounted for by the different course of the decrease of ΔS_H and ΔH_H with increase of ε.[141]

The quenching of ^3Q by primary and secondary aromatic amines in the case where ΔG_{23} is positive [for example in systems incorporating compound (IV) or (VIII) and DPA, 4-aminobiphenyl, or 4-bromoaniline] is accompanied by the formation of neutral radicals and takes place with rate constants exceeding significantly the analogous constants obtained for electron donors with the same oxidation potentials but without NH groups in their structure (Table 2).[42,89,90] It has been suggested that the quenching proceeds in accordance with Scheme (14), which includes the formation of a hydrogen-bonded TE ensuring very rapid transfer of a hydrogen atom.[42,89] The question of the degree of charge transfer in the hydrogen-bonded TE remains open; one must take into account the fact that the hydrogen bond reduces significantly the energy of the states with total charge transfer. The quenching rate constants increase with increase of ε of the medium or after the introduction of a solvating additive.[89] In a polar medium or under the conditions of specific solvation, the ΔG_{23} are lower and the reaction therefore proceeds in accordance with Scheme (12).

In certain cases the transfer of a hydrogen atom takes place also on quenching of ^3Q by tertiary aromatic amines, for example, in the compound (IV)—*NN*-diethylaniline system in benzene.[77] The existence of a fairly mobile proton in the amine radical-cation results in the appearance of a channel leading to the destruction of the polar TE—a proton transfer process. Direct observations by picosecond laser photolysis have shown that the proton transfer in the polar TE arising as a result of electron transfer from *N*-methylacridine to a molecule of compound (V) in the triplet state in benzene proceeds over a period of 140 ps.§

The formation of neutral radicals is frequently observed in the interaction of quinones in triplet states with aliphatic amines having a mobile hydrogen atom at the α-carbon atom. On quenching of the triplet state of compound (IV) by triethylamine, neutral radicals are formed in both non-polar and polar solvents.[77] In CINP experiments, it has been shown[117] that the photoinitiated transfer of a hydrogen atom in the compound (I)—triethylamine system in acetonitrile takes place in two stages.[117] This mechanism has been confirmed by direct observations for the systems compound (V)—triethylamine in toluene[111] and benzophenone—triethylamine system in acetonitrile.[142] When electron transfer is thermodynamically unfavourable, an effective transfer of a hydrogen atom as a whole can be achieved provided that the α-CH bond can be arranged parallel to the orbital of the unshared electron pair of the nitrogen atom.[143]

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§ See L.E.Manring and K.S.Peters, J.Amer.Chem.Soc., 1985, **107**, 6452.

The photolysis of quinones in the presence of aliphatic and secondary aromatic amines in frozen non-polar solvents is accompanied by the appearance of an EPR signal due to the pairs of neutral radicals formed on phototransfer of a hydrogen atom in the EDA complex.[144–146] The distance between the unpaired electrons in the radical pairs is 5–9 Å.

On the basis of the analysis of the temperature dependence of the yields of radicals of different nature in quinone–amine systems, one may expect that predominantly radical-ion pairs should be formed at low temperatures. However, this is true only in liquid solutions. In frozen solutions the formation of an ion pair may be difficult, since the rotational and translational mobilities of the solvent molecules are restricted, which hinders the reorganisation of the medium necessary for the stabilisation of the ion pair.

2. Interaction of Quinones in Triplet States with Phenols

The photoexcitation of quinonoid compounds in the presence of phenols is accompanied by the formation of semiquinone and phenoxy-radicals both in the liquid state and in a solid matrix. The kinetics and mechanism of the interaction of quinones in triplet states with phenolic compounds as well as the nature of the radicals formed have been investigated by flash photolysis,[41,42,84,89,90,147–165] EPR,[113,114,166] the CIEP method,[116,167–173] and the CINP method.[57,170,172,174–176] The steric structure and dynamics of the radical pairs formed in the photolysis of frozen solutions or crystals of quinones and phenols have been studied by EPR.[113,114,130,177–184]

(a) Kinetics of the reactions of quinones in triplet states with phenols. The quenching of the triplet states of quinones with a fairly high triplet energy by phenolic compounds takes place with high rate constants approaching the diffusional limit (65; see also Table 2).[42,57,84,149,150–152,163,167] As the electron-donating capacity of the phenol decreases, k_q initially falls but subsequently it begins to rise (Fig.5), which indicates a change in the reaction mechanism. The values of k_q diminish following the introduction of t-butyl groups in the *ortho*-position in the phenol owing to the shielding of the reaction centre.[151] Fig.5 shows that the quenching of the triplet state of anthanthrone, which has a low triplet energy, proceeds mainly with lower k_q (see also Table 2).[89,90,151] We may note that, although k_q diminishes as the electron-donating properties of the phenol are weakened, nevertheless the slope of the corresponding relations is significantly smaller than the value expected for electron transfer reactions and the k_q exceed the rate constant for electron transfer in the given systems. The observed set of characteristic features of the influence of the structure of the reactants and of the properties of the medium may be accounted for within the framework of three possible mechanisms [Schemes (12)–(14)].

The reactions between quinones in a high energy triplet state and phenols having fairly strong electron-donating properties (for example, hydroquinones) proceeds in accordance with Scheme (12); the protropic equilibrium in the radical pair is then fully displaced towards the formation of a pair of neutral radicals as a consequence of the extremely high acidity of the phenol radical-cations.

In the case where the free energy of the electron transfer from the phenol to the quinone molecule in the triplet state is large and positive, quenching takes place in accordance with Scheme (14). Hydrogen-bonded TE, in which the transfer of a hydrogen atom takes place, is formed in the first stage of the reaction. Since the triplet state is electrophilic, k_q diminishes as the electron-donating capacity of the phenol is reduced. An increase in the polarity of the medium weakens the hydrogen bond between the reactants in the TE, which is accompanied by a decrease of the rate constant for the transfer of a hydrogen atom.

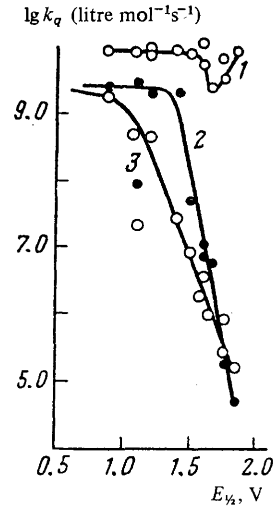


Figure 5. Dependence of lg k_q on the one-electron oxidation potentials $E_{1/2}$ of phenols in the quenching of the triplet states of 2,6-diphenyl-1,4-benzoquinone (energy of the triplet state ~2.3 eV) in benzene (curve *1*) and anthanthrone (energy of the triplet state ~1.6 eV) in benzene (curve *2*) and acetonitrile (curve *3*).[151]

It is noteworthy that the formation of a hydrogen bond in the TE can lead to a significant decrease in the energy of the state with total charge transfer (by approximately 1 eV and even more), which can be explained by the fact that the displacement of a proton from the donor to the acceptor is accompanied by an increase of the electron-donating capacity of the donor and of the electron-accepting capacity of the acceptor. For this reason, in hydrogen-bonded systems, where the free energy of the electron transfer calculated from the oxidation-reduction potentials of the reactants is positive, there is also a possibility of the transfer of a hydrogen atom via Scheme (12). The two-stage transfer of a hydrogen atom in certain analogous systems, where the reaction proceeds with participation of singlet hydrogen-bonded exciplexes, has been demonstrated experimentally as a result of direct observations by the method of picosecond laser photolysis.[185,186]

The quenching of ^{3}Q by phenols with very pronounced acid properties (picric acid, dinitrophenols) is described by Scheme (13). When this mechanism obtains, k_q can increase with increase of the acidity of the phenol and the polarity of the solvent as a consequence of the displacement of the prototropic equilibrium towards the ion pair.

The study of the influence of the viscosity of the medium on the kinetics of the quenching of the triplet state of anthanthrone by phenols made it possible to separate the stages involving the formation of a hydrogen-bonded TE and the transfer of a hydrogen atom in the TE.[90] The constants k_q

for certain phenols are significantly lower than the rate constant for the reaction occurring in each encounter of the reactants in solution, but they depend on the viscosity in the same way as the rate constant for a diffusion-controlled reaction (Fig.6). The rate-limiting stage of the reaction in these systems is the formation of a hydrogen-bonded TE. This process is controlled by the molecular mobility but takes place with a relatively low rate constant, since the formation of a hydrogen bonded complex requires a rigorous relative orientation of the reactants. An increase in the acidity of the phenol diminishes the rate constant for the formation of the intermediate hydrogen-bonded TE,[90] which can be explained by the fact that, in systems where a hydrogen atom is transferred in complexes with a stronger hydrogen bond, the reactants in these complexes are more rigorously oriented relative to one another and such "rigid" orientation hinders the formation of the complex.

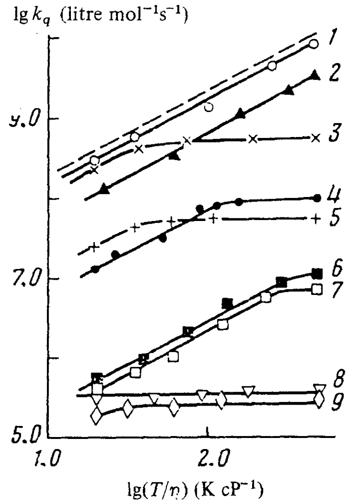


Figure 6. Dependence of lg k_q on lg (T/η) obtained in the quenching of the triplet state of anthanthrone in binary toluene–dinonyl phthalate and toluene–hexadecane mixtures by various compounds: *1*) *NN*-dimethyl-4-methoxyaniline; *2*) 2,4,6-trimethylphenol; *3*) 4-bromoaniline; *4*) 2,6-di-t-butyl-4-methylphenol; *5*) 2,3-dichlorophenol; *6*) 3-nitrophenyl; *7*) 4-nitrophenol; *8*) 4-methoxybiphenyl; *9*) 2,6-dinitrophenol. The dashed line has been calculated from the Debye formula ($8RT/3000\eta$).[90]

The nature of the rate-limiting stage and the mechanism of the quenching of ^{3}Q by phenols determine the observed kinetic isotope effect. The transfer of a hydrogen atom in the TE is characterised by an appreciable kinetic isotope effect, but when the rate-limiting stage of the quenching process involves the formation of an intermediate TE, no isotope effects are observed.[90,151] Low values (close to unity) of the kinetic isotope effect are characteristic also of quenching processes via Scheme (12) and (13), since the rates of these reactions are determined by stages involving charge transfer or the establishment of protropic equilibrium.[89,151]

(b) The formation of radicals in the photolysis of quinones in the presence of phenols. In most systems, the interaction of quinones in triplet states with phenols leads to the formation of semiquinone and phenoxy-radicals in yields close to 100%,[42,89,149,151] but CINP studies on the photolysis of quinones in the presence of phenols indicate an insignificant contribution to the geminal radical pair recombination process,[57,170–172,174–176] which should reduce the yield of radicals. Furthermore, if the process is described by Scheme (12), the decrease in the yield of radicals may be caused by rapid intersystem crossing in the non-equilibrium TE. Thus relatively low yields of radicals in the quenching of the triplet state of chloranil (II) by tetrachlorohydroquinone can be explained in this way.[41,152]

Very low yields of radicals have been observed in the quenching of the triplet state of anthanthrone by picric acid and dinitrophenols in benzene.[151] The reaction in these systems is described by Scheme (13) and the main channel leading to the destruction of the radical pair, formed after proton transfer, is the intersystem transition to the ground state. If the proton transfer reaction in the primary TE competes with the hydrogen atom transfer, then the yield of phenoxy-radicals increases with increase of temperature as a consequence of the shift of the prototropic equilibrium towards the primary TE in which the hydrogen atom is transferred.[151] The existence of the prototropic equilibrium also explains the low yields of radicals (which increase with increase of temperature) in the quenching of polar TE by phenols.[163] The transfer of a hydrogen atom results in the formation of a complex incorporating the phenoxy- and semiquinone radicals and also a molecule of the electron donor (amine). The prototropic equilibrium in this complex is determined by the proton transfer between the amine and the semiquinone.

It has been noted that, in the quenching of ^{3}Q having non-equivalent oxygen atoms, the formation of two types of semiquinone radicals may be expected, their ratio of their yields depending on the reaction mechanism.[151]

Photolysis of frozen solutions of phenols and quinones leads to the formation of radical pairs from phenoxy- and semiquinone radicals.[113,177] The phototransfer of a hydrogen atom takes place in EDA complexes, which are also present in aqueous solutions, this being indicated by the slight scatter of the distance between the unpaired electrons in the radical pair ($\leq$0.1 Å).[177,179] Estimation of the formation constant for these complexes yields 0.2–3 litre mol^{-1} at −90 °C.[181] Analysis of the EPR spectra yielded geometrical parameters characterising the relative disposition of the radicals in the pair—the planes of their rings are parallel and are located at a distance of 1.6 Å.[180] At a low temperature the radical pairs rotate as a whole with characteristic times in the range 0.1–1.0 ms.[182]

Two types of radical pairs with different distances between the unpaired electrons have been detected for o-benzoquinone derivatives, which has been explained by the migration of the proton in the semi-quinone between two non-equivalent oxygen atoms.[177–180,182,184] The formation of two types of radical pairs can also be caused by the existence of EDA complexes of different composition.[183]

Two types of EPR signals of the radical pairs have been recorded in the photolysis of single crystals in polycrystalline specimens of 3,6-di-t-butyl-1,2-benzoquinone and the corresponding catechol.[129,130] One type has been assigned to the radical ion pair and the other to the pair of neutral radicals. These radical pairs are formed and are destroyed independently of one another. Presumably the protropic equilibrium in the crystal is frozen and the hydrogen atom and electron transfer processes therefore proceed in parallel within donor and acceptor pairs, whose structure and molecular environment favour either the transfer of a hydrogen atom or the transfer of an electron. Electron transfer has been postulated in the photoexcitation of the EDA complex of duroquinone and hydroduroquinone in the region of the CT band in alcohol.[187]

3. The Abstraction of a Hydrogen Atom by Molecules of Quinones in The Triplet State from Other Organic Compounds

The transfer of a hydrogen atom to ^{3}Q is a very common reaction and is observed in interactions with hydrocarbons, ketones, ethers, aldehydes, anhydrides, and amides—virtually with participation of all organic compounds.[4–6]

The molecules of quinones in the triplet state can abstract a hydrogen atom even from benzene, although the quantum yield in the formation of radicals is very low.[39,188–191] The rate constant for the quenching of the triplet state of compound (V) by benzene in CCl_4 is 7.2×10^5 litre mol^{-1} s^{-1} and increases to 2.2×10^6 litre mol^{-1} s^{-1} on passing to acetonitrile.[192] The nature of the triplet state is very important in the reaction with benzene; thus the rate constants for the interaction of derivatives of compound (V) having a triplet state of the $n\pi^*$ type with benzene are significantly lower.[192] The transfer of a hydrogen atom from benzene takes place in a non-polar TE (of the type of a biradical adduct[57]) and is a side channel leading to the destruction of this species.

The photochemical reduction of quinones in a mixture with saturated hydrocarbons is relatively ineffective;[78,150,193] nevertheless, it has been possible to detect radicals by EPR[194] and flash photolysis.[39,149,195–198] The quantum yield of the radicals in the photochemical reduction of compound (IV) in cyclohexane is only 0.09[149] and is even lower in hexane.[78,150] In the case of compound (V), which has a triplet state of the $n\pi^*$ type with a higher energy, the quantum yield of the radicals in hexane is 0.11,[196] while $k_q = 8.6 \times 10^5$ litre mol^{-1} s^{-1}.[199]

The reactivity of ^{3}Q in relation to alkylbenzenes, fluorene, and 9,10-dihydroanthracene has been investigated in detail.[200–206] The rate of disappearance of 9,10-phenanthrenequinone (X) increases in the sequence benzene < t-butylbenene < toluene < ethylbenzene < cumene (0.33, 0.42, 1.00, 1.27, and 2.33 respectively).[200] It has been established by the CINP method that the primary step involves the abstraction of a hydrogen atom in α-position in the alkyl substituent with formation of radical pairs, which give rise to adducts on formation of C–C or C–O bonds.[201–206]

Experiments on picosecond laser photolysis demonstrated that a hydrogen atom is transferred from durene to a molecule of chloranil in the triplet state via Scheme (12) in a non-equilibrium polar TE.[48] A small contribution by a slow proton transfer process in the equilibrium TE has also been observed.

In the photolysis of frozen solutions of *p*-benzoquinone and alkylbenzenes on irradiation in the region of the CT band, the formation of radical pairs in the triplet state, incorporating neutral radicals with the distance between the unpaired electrons in the range 5.8–6.1 Å has been noted.[38] The radical pairs are also formed in the compound (I)–α-methylnaphthalene system but not in the system with β-methylnaphthalene, which is due to the different relative positions of the reacting groups (for example, the greater distance of the methyl group from C=O in the EDA complex with β-methylnaphthalene).

It has been shown by flash photolysis that radicals are formed in the photolysis of compound (IV) in chloroform[197] and of compound (II) in 1,2-dichloroethane; the quantum yield is 0.19.[40] It follows from CINP data that the reaction of fluoroanil in the triplet state with chloroform includes a stage in which a radical pair is formed. The latter then recombines to the initial reactants and dissociates into radicals.[57,175,176] A study of the reaction by EPR showed that the effectiveness of the formation of the radicals increases in the presence of traces of acid.[207] Presumably the transfer of a hydrogen atom includes a proton transfer stage.

The formation of semiquinone radicals has been observed in the photolysis of compound (II) in acetonitrile and propionitrile together with charged radicals;[39,40,83,108,110] the yield of radicals in propionitrile is then higher than in acetonitrile.[83] However, it has been concluded that semiquinone radicals are not products of the reaction of compound (II) in the triplet state with solvent molecules but are formed in photochemical side reactions.[108,110]

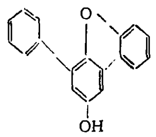
A hydrogen atom is transferred extremely effectively in the reactions of ^{3}Q with olefins. The rate constant for the quenching of the triplet state (X) by 2-methylpropene, *trans*- and *cis*-but-2-enes, 2-methylbut-2-ene, and 2,3-dimethylbut-2-ene in benzene increases from 1.0×10^8 to 1.3×10^9 litre mol^{-1} s^{-1} in this series of compounds.[208] The quantum yield of the reaction then increases from 0.21 to 0.79 and there is a simultaneous increase of the contribution of the R–H addition process, which includes a hydrogen atom transfer stage. A hydrogen atom is transferred in the TE and this process competes with the other TE destruction channel—the formation of cycloaddition products. The formation of various adducts in the TE and in the pair of neutral radicals leads to a low yield of radicals. The quantum yields of semiquinone radicals when the triplet stage of chloranil is quenched by acrylonitrile and methyl methacrylate in 1,2-dichloroethane are 0.2 and 0.08, while radicals were not detected in the quenching by styrene.[40] The quenching rate constants are determined by the ionisation potential of the donor (Table 2).

In the interaction of ^{3}Q with ethers, a hydrogen atom is transferred from the α-position. Radicals have been detected by EPR,[172,190,207,209–216] and flash photolysis.[39,41,215] According to CINP data, the radical pair recombines to adducts.[172,202,203,205,206,217–220] The reactivity of ethers is higher than that of alkylbenzenes. The rates of disappearance of compound (X) in tetrahydrofuran, dioxan, and diethyl ether are 1.78, 2.47, and 3.44 respectively (relative to toluene),[200] which is due to the presence of the oxygen atom with the unshared electron pair participating in the electron donor–acceptor interaction with ^{3}Q in the TE. A hydrogen atom may be transferred on irradiation with light in the region of the CT band in the spectrum of the EDA complex in the triplet state, as has been observed in systems of the type $R{-}X{-}CH_2CO_2H$ (X = O, S, or NH)[221] or in the compound (II)–dioxan system.[41] The yield of radicals in the latter case is 0.13, the rate constant for the formation of radicals from the TE is 3.8×10^4 s^{-1}, and the rate constant for other TE deactivation processes is 2.6×10^5 s^{-1}.

Semiquinone radicals have been recorded by EPR[190,207,209,212,214,222] and by flash photolysis[39,105,110] on photoexcitation of quinones in acetone. The yield of radicals increases in the presence of traces of acids.[207] It has been suggested that semiquinone radicals are formed in a photochemical reaction with participation of the products of a dark reaction between the reactants.[108,110]

The molecules of quinones in triplet states abstract a hydrogen atom from the aldehyde group.[4] The reaction has been investigated by the CINP method and it has been shown that its mechanism is the same as for processes involving the participation of ethers and alkylbenzenes.[206] The reactions involving the abstraction of a hydrogen atom from anhydrides and amides are also known.[4] In the case of amides[4] and phosphates[190,210,212,214] semiquinone radicals have been detected by EPR. Semiquinone radicals are formed on photoexcitation of quinones in microemulsions[104] and in micellar solutions[223–227] as a consequence of the transfer of a hydrogen atom from the surfactant.

There exist numerous photochemical reactions of quinonoid compounds with participation of their substituents. It has been frequently suggested that the primary process is the transfer of a hydrogen atom from the substituent to the carbonyl oxygen atom, but this mechanism is still controversial.[4] A solvent molecule can participate in reactions of this type. For example, the formation of the final product of the photolysis of compound (III), i.e.



can also be accounted for within the framework of the mechanism involving intramolecular transfer of a hydrogen atom, but CINP data showed that the primary step is electron or hydrogen atom transfer from the medium with subsequent abstraction of a hydrogen atom from the substituent in the quinone by a solvent radical.[228,229]

V. PRIMARY PROCESSES IN THE PHOTOCHEMICAL REDUCTION OF QUINONES BY ALCOHOLS

Numerous studies have been devoted to the mechanism of the photochemical reduction of quinones in alcohols; the problem of the nature of the primary step, whether it is electron transfer or the transfer of a hydrogen atom as a whole, has been discussed in many of them.

The photolysis of frozen alcoholic solutions of quinones leads to the formation of semiquinone radicals, detected by UV absorption or by EPR.[38,222,230–235] The study of the nature of the alcohol radicals has shown that alkoxy-radicals are formed initially.[230,232] The primary step is electron transfer with subsequent proton transfer from the hydroxy-group. Hydroxyalkyl radicals are formed in secondary reactions. There exists a second reaction channel—the abstraction of a hydrogen atom from a carbon atom; the contribution of this pathway is 10% in the compound (I)—ethanol system.[222]

The intermediates in the photochemical reduction of quinones in the presence of alcohols in liquid solutions have been investigated by flash photolysis.[39,78,81,93,105,149,150,215,229,236–248] Scheerer and Grätzel[78] concluded that a molecule of compound (IV) in the triplet state abstracts an electron from an alcohol molecule in the 2: 1 water–ethanol mixture. The formation of radical-anions derived from compound (IV) with a quantum yield of 0.2 is observed simultaneously with the destruction of the triplet. The photolysis of compound (II) in ethanol takes place analogously.[7] The interaction of compound (IV) in the triplet state with the solvent in ethanol and isopropyl alcohol leads to the formation of semiquinone radicals with a yield of 0.4.[149,150] Semiquinone radicals are formed in high yields (up to 1.0) in many other systems, but a hydrogen atom can then be transferred via a two-stage mechanism.[229]

Convincing conclusions concerning the mechanisms of the interaction of compound (V) and its halogeno-derivatives with ethanol have been reached in a study[192]¶ of the influence of added acid on the isotope effect in the photochemical reaction. Simultaneous formation of a radical-anion and the semiquinone radical was observed. Deuteriation of the alcohol reduces the yield of the photochemical reduction reaction by a factor of 1.5. The introduction of CF_3COOH does not influence the isotope effects in the case of compound (V) but reduces the isotope effect in reactions involving the halogeno-derivatives, which have a lowest triplet state of the $\pi\pi^*$ type. Thus the molecule of compound (V) in the triplet $n\pi^*$ state abstracts a hydrogen atom from an ethanol molecule, while the halogeno-derivatives of compound (V) in the triplet $\pi\pi^*$ state abstract an electron with subsequent proton transfer. Comparison of the quantum yields in the photochemical reduction in C_2H_5OD and C_2D_5OH showed that the proton is transferred from the α-carbon atom of the alcohol radical-cation.

The rate constant for the quenching of the triplet state of compound (IV) by ethanol and isopropyl alcohol is 3×10^4 litre mol^{-1} s^{-1},[78,249] while that for the quenching by benzyl alcohol is 8×10^5 litre mol^{-1} s^{-1} and increases to 2.7×10^7 litre mol^{-1} s^{-1} on protonation of a molecule of compound (IV) in the triplet state,[81] which suggests electron transfer. A significant increase in the rate constant for the quenching of ^3Q by alcohols has been observed on passing from quinones with lowest triplet states of the $\pi\pi^*$ type [compounds (II), (III), and (IV)] or of the CT type (2-piperidino-9,10-anthraquinone) to quinones with triplet states of the $n\pi^*$ type [compounds (I) and (V)]. In the quenching of compound (V) in the triplet state, the constant k_q ranges from 3×10^6 to 2×10^7 litre mol^{-1} s^{-1},[199,250] while an estimate of k_q for the quenching of compounds (I) in the triplet state by methanol in water yielded a value in excess of 10^8 litre mol^{-1} s^{-1}.[242] This feature indicates a radical mechanism of the reaction, on the basis of which the activity series of alcohols in their photochemical dehydrogenation, which is determined by the mobility of the hydrogen atom in the α-position, has been explained.[251]

The mechanism of the photochemical reduction of quinones by alcohols has been investigated by the CIEP[116,119,167,169,171,173 252–260] and CINP[170,228,229,253,261–264] methods, which in most cases do not yield an unambiguous answer as to the nature of the primary radicals. The conclusion that the primary step is electron transfer was reached in a CINP study in the compound (I)—CCl_3COOH–t-butyl alcohol[263] and compound (III)—n-propyl alcohol[228,229] systems in which CINP arises via a triplet mechanism whose manifestation is possible by virtue of the short electronic relaxation time of the alcohol radical-cation. The study of the latter system simultaneously by the CINP and flash photolysis methods showed that, although the primary step is electron transfer, ultimately neutral radicals emerge from the solvent "cage" owing to the subsequent proton transfer.

The nature of the radicals formed in the photolysis of alcoholic solutions of quinones has been investigated in detail by EPR.[167,189,190,207,210,212,214,215,265–276] Using spin-trapping agents, it has been possible to detect primary (very short-lived) alkoxy-radicals derived from the alcohol.[187,271,272,276] It was concluded that the primary step is in many cases electron transfer. In the case of very distinct triplet states of the $n\pi^*$ type there exists a second reaction pathway—the transfer of a hydrogen via a radical mechanism. The transfer of an electron or a hydrogen atom takes place in a hydrogen-bonded

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¶ See also K.Hamanoue, K.Yokoyama, Y.Kajiwara, K.Nakajima, T.Nakayama, and H.Teranishi, Chem.Phys.Letters, 1984, **110**, 25.

EDA complex in the triplet state and is induced by the electron donor–acceptor interaction with participation of the unshared electron pair localised on the oxygen atom of the alcohol molecule and the electron located in the *n* orbital of the quinone molecule in the triplet state.

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Analysis of the literature data permits the conclusion that the electron transfer processes and the formation of triplet electron donor-acceptor complexes with a particular degree of charge transfer and with a hydrogen bond play an important role in the photochemistry of quinonoid compounds. The kinetics and mechanism of the formation of triplet exciplexes and the processes occurring in them constitute a basis which determines the course of the subsequent chemical reaction. The study of the physicochemical properties of triplet exciplexes constitutes an important field in photochemistry.

Triplet exciplexes are not formed as intermediate species in many photochemical and photobiological systems alone. Modern approaches to the creation of new methods for the recording of information on non-silver materials can also include exciplex systems in which triplet exciplexes play a key role. By virtue of the progress in the field of new methods based on laser techniques, this field is developing rapidly at the present time.

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Advances in the Study of Metal Complexes with Tervalent Phosphorus Amides

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Data on the synthesis, structure, and chemical properties of complexes of non-transition and transition metals with tervalent phosphorus amides are surveyed. An attempt is made to trace the influence of the amide functional group of the ligand on the properties of these compounds. The literature data on the practical use of the metal complexes with formamides are analysed in the review.

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I. INTRODUCTION

The metal complexes of ligands containing a tervalent phosphorus atom are being vigorously investigated. Studies have been made of their synthesis, structure, physiological activity, chemical properties, and catalytic properties. Analysis of the existing publications has shown that the vast majority of the latter are devoted to complexes with phosphine ligands, namely with triphenylphosphine. Apparently, the availability of triphenylphosphine, the convenience with which it can be employed, as well as Wilkinson's succesful synthesis of effective catalytic systems based on this phosphine, dictated the choice of the ligands. Overall, the tendency to employ a narrow group of well known ligands arose from the passive attitude of organophosphorus chemists to the new field in the boundary region where the interests of coordination chemistry and the chemistry of organophosphorus compounds are interlinked. In recent years the situation changed and complexes with a wide variety of phosphorus ligands—phosphites, phosphonites, phosphinites, phosphorofluoridites, etc.—began to be investigated and fundamentally new results have been obtained. Together with the ligands already enumerated, tervalent phosphorus acid amides (TPAA), which are very interesting from the chemical standpoint, began to be used as ligands. Initially such derivatives were regarded as kinds of "hybrids" of two popular classical ligands—phosphines and amines. Subsequently, novel qualities of formamides, which make the complexes obtained from them very unusual, were discovered.

The field of science devoted to the study of metal complexes of TPAA is at present still in the stage of its establishment. More than 350 articles and patents have been devoted to it. However, it is significant that the existing publications do not as yet constitute a stream of relevant information and chemical ideas. As a rule, they report only new facts which are not compared to any great extent with facts known from related studies and studies on other phosphorus-containing complexes. In view of this, we aimed to prepare the first review in the world literature on metal complexes of TPAA. For this purpose, we have given a systematic account of published data and have analysed (insofar as this is at present possible) the influence of the phosphamide fragment of the ligand on the synthesis, structure, and properties of new coordination systems. It is essential to note the characteristic feature of this review. The relevant problems are considered from the standpoint of organophosphorus chemistry which in our view should have full parity with coordination chemistry in the study of the systems mentioned.

II. SYNTHESIS

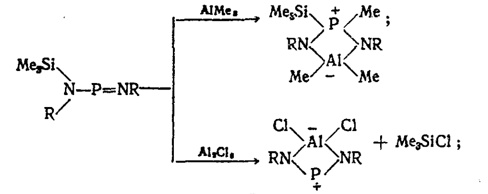
1. Non-transition Metal Complexes

There are only very brief mentions in the literature of the preparation of complexes of TPAA with zinc and cadmium. The complexes $ZnCl_2L_2.2H_2O$ have been obtained from the triethyleneamide of phosphorous acid.[1] The mode of coordination and other structural problems have not been reported. The reactions of the hexamethyltriamide of phosphonous acid (I) and of the tetramethyldiamide of phenylphosphonous acid (II) with CdI_2 have been described;[2] according to the authors, the products $CdI_2.(I)_2$ and $CdI_2.(II)_2$ were obtained. It has been assumed[3] that the coordination of the ligand in the interaction of $Cd(NO_3)_2$ with the di(butylamide) of cyclohexylphosphonous acid is effected via the unshared electron pair of the nitrogen atom. We may note that the structures were not rigorously demonstrated in the above studies.[2,3]

The complexes of bivalent mercury with mono- and bi-dentate ligands have been investigated in greater detail.[2,4-7] It has been established that compounds having the compositions HgX_2L_2 and HgX_2L can then be formed. The coordination of the ligands to the phosphorus atom was elucidated on the basis of ^{31}P NMR data and in addition the *trans*-configuration of the complexes HgX_2L_2 was demonstrated. The formation of the mercury complexes can be accompanied by unusual reactions, for example, the formation of P—P bonds.[2]

Among Group III metals, only aluminium has been studied in reactions with TPAA. Vigorous complex formation by triethylaluminium via phosphorus in interaction with equimolar amounts of amides or imides or phosphinous acid has been demonstrated.[8] In the latter case adducts were obtained in which the two phosphorus atoms are equivalent according to NMR data, indicating the parallel binding of the aluminium atom with two phosphorus atoms. When *HN*-phosphimides are used, the complex formation reaction is supplemented by the metallation of nitrogen. TPAA react also with $AlCl_3$: the formation of monoadducts in this process has been indicated.[9] On dissolution in methylene chloride, the latter can react with formation of phosphorus–phosphorus systems.[10,11] The reaction dynamics has been investigated by ^{31}P NMR. Analogous derivatives can be more simply obtained by the reaction of $AlCl_3$ with phosphoramidochloridites, Salts whose cations have a discoordinate phosphorus atom are then formed initially. Subsequently, they disproportionate or add to the electron-donating TPAA.[9,10,12]

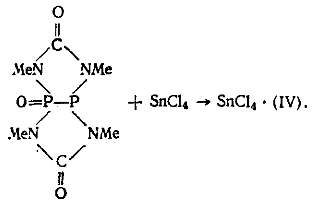
Very interesting results have been obtained[13,14] in the study of *N*-silylated amides of phosphorimidic acids (III):



R=SiMe₃, Bu-t.

The difference between the reactions of the amidoimide (III) with trimethylaluminium and trimethylboron is noteworthy; the latter reaction leads only to a linear system with the boron atom at one of its ends.[14]

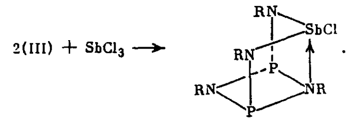
The wide-scale study of the synthesis of phosphorus complexes based on tin halides has been initiated. Compounds having the composition $SnCl_4L_2$ have been obtained from the full amides and amidoesters of phosphorous acids[15,16] and the amides of phosphonous[17,18] acids. The complex $SnCl_4L$ has been synthesised from the complex P–P ligand (IV):[19]



(IV)

The study of the structure of the complexes by ^{31}P NMR, ^{1}H NMR, and infrared spectroscopy led to the conclusion that the ligand is coordinated to the phosphorus atom. It has been shown that the stability of the test substances is determined by the electron-donating capacity of the substituents at the phosphorus atom.[16]

Derivatives of Group V non-transition metals have been little studied in their complex formation reactions with TPAA. It has been reported that $SbCl_5$ chlorinates these compounds, being reduced at the same time to $SbCl_3$. The second stage of the process involves the formation of aminochlorophosphonium hexachloroantimonates.[20] Furthermore, the possibility of the usual complex formation reaction between $SbCl_5$ and the P–P ligand (IV) has been indicated.[19] An unusual reaction involving a stage in which the nitrogen atom of the phosphamide centre is coordinated to SbCl has been described:[21]



The mode of coordination is determined by stereochemical factors, namely by the mutual approach in space of the antimony and nitrogen atoms. The use of $AsCl_3$ does not lead to the closure of the skeletal system.[21]

2. Transition Metal Complexes

The study of transition metal complexes with TPAA was begun comparatively recently, but it is being prosecuted vigorously and is distinguished by highly novel synthetic features. One may say that a much greater number of different types of complexes have been created in this field than in other related fields of coordination chemistry. This situation can apparently be accounted for by the structural variety of the ligands related to TPAA and the wide variety of their chemical properties: the synthesis of complexes of each group will accordingly be considered in a way emphasising the role not only of the metal but also of the corresponding type of phosphamide ligand.

The complexes of metals of the first Groups have been investigated relatively modestly. On the other hand, those of Group VI, VII, and VIII metals have been widely studied and the characteristic features of the individual classes of compounds have been elucidated.

(*a*) *Complexes of metals in the first Groups.* Among the phosphamide complexes of copper, silver, and gold, derivatives of univalent copper have been investigated in greatest detail. The first representatives of compounds of this class have been obtained[22] by the interaction of the salt CuX with the simplest amides of alkylene phosphorous acids. Subsequently the reaction was extended to a wide range of phosphamides,[4,23,24] including cyclic phosphoramidites of carbohydrates.[25,26] The structures of the majority of the complexes obtained have been investigated by NMR and X-ray diffraction, which demonstrated that the ligand is coordinated to the phosphorus atom. In complexes of the phosphorinane type, it was shown that the metal occupies an axial position and that the six-membered ring has the chair conformation.[24]

Certain phosphamide complexes of copper hydride[27] and organocopper compounds[28] have also been studied.

Silver complexes of different composition have been obtained by the reaction of the salts AgX with the phosphamide (I). When X = Cl, CN, or NO_3, the compounds $AgXL_2$ are formed and, in the case where X = BPh_4, systems in which three molecules of the ligand (I) are incorporated in the central nucleus can be isolated. The same picture has been noted in a study with the bicyclic compound $P(NMeCH_2)_3.CMe$ (V) using salts with different anions. The triethyleneamide of phosphorous acid gives rise to the complexes $AgXL_4$ regardless of the type of anion. In all cases the ligand is coordinated to the phosphorus atom, which has been demonstrated by X-ray diffraction.[29] The difference noted in the behaviour of formally similar ligands is apparently associated with the appreciable difference between their geometrical parameters and the wide variety of the electronic effects in the P–N fragment.[30] In confirmation of the latter postulate, we may note that sterically hindered phosphamides are only singly bound to silver salts.[31]

Bidentate ligands have also been investigated in reactions with silver salts.[6,32] The iminodiphosphines (VI) have been studied in special detail:[32]

$$MeN(PPh_2)_2 + AgBr \rightarrow [MeN(PPh_2AgBr)_2]_2 .$$

(VI)

The structure of the adduct whose molecule is based on the $Ag_4Br_2^{2+}$ octahedron has been demonstrated by X-ray diffraction. We may draw attention to the specific influence of the amide unit, manifested in the formation of the octahedral structure. If instead of this unit, two phosphorus atoms are linked by a methylene group, a different polyhedron, namely $Ag_3Br_2^{+}$, is formed.[32]

Complexes of univalent and tervalent gold with TPAA began to be investigated only in very recent years. The amides of phosphinous acids[31] and azaphospholes[33] have been used as monodentate ligands. The problem of the mode of coordination of the ligand still remains controversial in this instance. Iminodiphosphines[34] and the corresponding anions[35] have been used as bidentate ligands.

The study of the complexes of TPAA with Group IV and V metals has been fragmentary. There exists a brief communication about the chelation of the central atom in $TiCl_4$ by 1,3-di-t-butyl-2,4-dichloro-1,3,2,4-diazadiphosphetidine (VII).[36] There has been a very interesting study of the oxidative addition of phosphorous acid triisocyanate to $TiCl_4$ and $ZrCl_4$:[37]

$$MCl_4 + P(N{=}C{=}O)_3 \rightarrow MCl_3P(N{=}C{=}O)_2 + ClN{=}C{=}O\,.$$

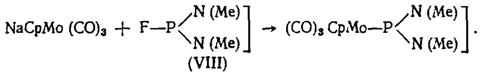
The diethylamides of dimethyl phosphorous and phenylphosphonous acids add to VCl_4; 1 : 1 and 2 : 1 adducts are formed in the former case and only 1 : 1 atoms in the latter.[38] A series of complexes have been synthesised by ligand transfer reactions between $CpV(CO)_3L$ and the full amides of phosphorous,[39,40] and dimethylphosphinous[41] acids:

$$CpV(CO)_4 + L \rightarrow CpV(CO)_3L\,.$$

$CpNb(CO)_4$ reacts in accordance with an analogous scheme but with more extensive substitution.[42]

(*b*) *Complexes of Group VI metals*. Almost all the studies published on this question have been devoted to the derivatives of metals in the lowest oxidation states. A common feature of these investigations is the use of identical or structurally similar initial metal-containing compounds. These are usually hexacarbonyls or mixed carbonyls. The substances mentioned are made to react with TPAA and one mole of carbon monoxide is readily evolved.† When special rules are fulfilled, even more complete substitution of the carbonyl ligand may take place. Acetonitrile, olefins, etc. are displaced from the coordination sphere more readily than carbon monoxide. The principle of ligand displacement constitutes the basis of the most popular direct method of synthesis of the complexes considered. However, this method can be supplemented successfully in many instances by a second, combined procedure. Complexes of the metal with phosphorus acid chlorides or other phosphorus compounds capable of reacting with nucleophiles are obtained in a preliminary step. In the concluding stage the intermediate complexes are made to react with nitrogen-containing bases to form the required products.

Direct synthesis. Chromium and molybdenum complexes may be obtained by electrophilic substitution at the metal atom, i.e. by the reaction of carbonylate anions with aminohalogeno-derivatives of phosphorous acid.[43-45] Substitution takes place readily, since the aminohalogeno-derivatives, especially 2-fluoro-1,3-dimethyl-1,3,2-diazaphospholan (VIII), readily give rise to highly electrophilic phosphamide cations. This results in the formation of phosphometallic systems, for example:



(VIII)

$$NaCpMo(CO)_3 + \left[F{-}P\begin{matrix}N(Me)\\N(Me)\end{matrix}\right] \rightarrow \left[(CO)_3CpMo{-}P\begin{matrix}N(Me)\\N(Me)\end{matrix}\right].$$

The chemical structure of the substances obtained has been demonstrated by X-ray diffraction. The final conclusion about the electronic structure has not yet been reached, although this problem is the subject of a lively discussion.[45,46]

Carbonylate ions have been made to interact with the tetrafluoride of *N*-methyldiphosphorimidic acid (IX):[47]

$$\underset{(IX)}{MeN(PF_2)_2} + NaCpMo(CO)_3 - \begin{cases} \xrightarrow{1:1} F_2PN(Me){-}PF[MoCp(CO)_3]\,; \\ \xrightarrow[1:2]{} F_2PN(Me){-}P[MoCp(CO)_3]_2\,. \end{cases}$$

The reaction proceeds in a more complex manner in another instance:[48]

$$(Me_3Si)_2NPCl_2 + Na_2Cr(CO)_5 \rightarrow Cr(CO)_5[P{-}N(SiMe_3)_2]_2 +$$
$$+ [Cr(CO)_5]_2PN(SiMe_3)_2 + \{Cr(CO)_4[PN(SiMe_3)_2]_2\}[Cr(CO)_5]_2\,.$$

All the substances indicated have been isolated from the reaction mixture by fractional recrystallisation and their structures have been determined by X-ray diffraction. The chemistry of these reactions has not been discussed. Carbonylate anions have been made to react with the aminofluoroderivatives of phosphorous acid in the presence of mercury(II) chloride, which is an oxidant. Derivatives of zero-valent metals are formed in this case:[49]

$$M_2(CO)_{10}^{2-} + F_2PNEt_2 + HgCl_2 \rightarrow M(CO)_5(F_2PNEt_2)\,;$$
$$M{=}Cr,\ Mo,\ W\,.$$

TPAA manifest much more frequently only a ligand transferring activity without the loss of their structural elements, as shown above. We shall consider this possibility in relation to the employment of derivatives of zero-valent metals of different chemical nature—neutral complexes of the type $M(CO)_6$, ionic complexes of the type $[M(CO)_5X]^-$, and other related compounds. These substances effectively undergo ligand transfer reactions with full amides,[1,5,50-55] ester amides,[56] mixed amide–acid halides,[5,57-59] and imino-amides [60,61] of phosphorous acid, the amides of phosphonous and phosphinous acids,[23,41,50,60,62,63] diazaphospholes,[64] and the amides of hypodiphosphorous and other branched P–P acids.[19,65-67] The amides of diphosphonous acids and other bidentate ligands[68-72] as well as cyclic[73,74] and bicyclic[51,56,75] phosphamides play an important role in these reactions.

Monosubstitution of the carbonyl ligand takes place under relatively mild conditions. For this purpose, metal hexacarbonyls or other related substances are heated with an equimolar amount of TPAA in an organic solvent.[41,56,60,76-78] It is useful to carry out the reaction in its photochemical version:[49]

$$M(CO)_6 + THF \xrightarrow{h\nu} M(CO)_5 \cdot THF \xrightarrow{L} M(CO)_5L\,.$$

In studies with enantiomeric TPAA and prochiral complexes, diastereoisomers were synthesised[61,62,79] and it proved possible to separate them by the usual methods.

The reactions of ligands with molecules containing two phosphorus atoms, including phosphorus atoms linked directly to one another, have been investigated in various laboratories. If one of these atoms is tervalent and the other pentavalent, the process takes place only once.[19] If both phosphorus atoms are tervalent, as in the ligand (X), then the monosubstitution of the metal can proceed with participation

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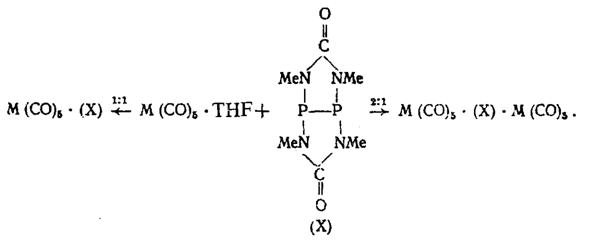
† In the interaction of ionic reagents, carbon monoxide may not be evolved.

of one or both[65,67] phosphorus centres:



(X)

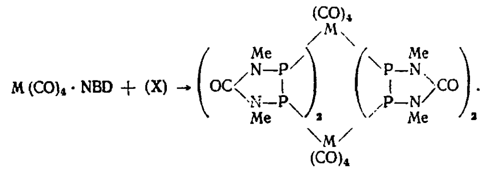
An analogous situation arises in diazadiphosphetidines.[73,77]

In the reactions examined above the difference in the complex formation reactions of chromium, molybdenum, and tungsten carbonyls was hardly manifested. Nevertheless, such a difference can be found by analysing the reactions of these carbonyls with the bidentate phosphimide ligand $(Ph_2P)_2NCH(R)COOMe$ (XI). Tungsten carbonyls react mainly with monosubstitution, while chromium and molybdenum carbonyls react with disubstitution.[80,81]

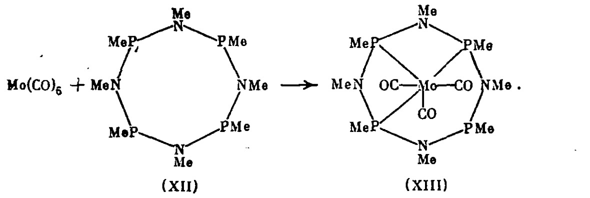
The bis-ligand transfer reaction has also been studied in detail. In order to achieve a satisfactory result, an excess of the ligand is normally employed.[5,52] The synthesis of disubstituted products is of special interest since generally speaking it can lead to geometrically isomeric complexes. It has been noted that the *cis*-forms are formed preferentially in the initial stage and can be converted on heating into the *trans*-forms.[5,57,59] In a number of experiments it proved possible to separate these isomers and to investigate their specific properties.[5,52]

It is essential to consider specially the ligand transfer reactions of phosphamides with other electron-donating centres. The hydrazide of diphenylphosphinous acid reacts with metal hexacarbonyls to form chelates.[82] An analogous result has been achieved with the full amides of αω-alkylenediphosphonous acids. When the distance between the phosphorus atoms in the molecules of the latter reaches a specific value, dinuclear systems are formed.[68,69,72]

Iminodiphosphine ligands of types (VI), (IX), and (XI) have been studied more widely in metallocycle formation.[80–86] Interesting results have also been obtained for the interaction of the norbornadiene (NBD) complexes of chromium and molybdenum carbanions with the P–P ligand (X):[67]



The tris-ligand transfer reaction has been studied relatively little. In relation to metal hexacarbonyls, this reaction yields positive results only when a specific TPAA are used. Such a ligand is the eight-membered phosphazane (XII):[87]

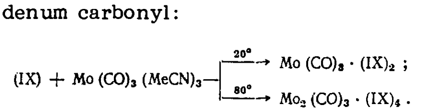


(XII) (XIII)

The fourth phosphorus atom is not coordinated to molybdenum. It is of interest that this phosphorus atom forms the longest bonds with the neighbouring nitrogen atoms (1.742 and 1.728 Å); the lengths of other bonds in the ring are much shorter (1.699 and 1.712 Å). The phosphorus atom not involved in coordination has the smallest endocyclic angle (107.13° against 109.02–110.5°).

On reaction with MeI, the neutral compound $(MeNPMe)_4.Mo(CO)_3$ (XIII) forms the corresponding ionic complex, which can also be prepared by the reaction of the ligand (XII), MeI, and $Mo(CO)_6$.

A study of the tris-ligand transfer reaction of hexacarbonyls with the dimethyl hydrazide of diphenylphosphonous acid has been published.[82] The ligand is bound in this reaction to the metal only via the phosphorus atoms. Nevertheless, in synthesis involving phosphorylated α-aminopyridine, coordination with participation of both the phosphorus atoms and the nitrogen atoms of the pyridine rings has been noted.[89,90] Very interesting results have been obtained[91] in a study of the interaction of the bidentate ligand (IX) with a mixed molybdenum carbonyl:

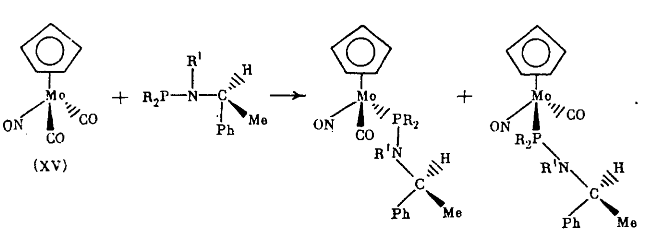


$$(IX) + Mo(CO)_3(MeCN)_3 \begin{cases} \xrightarrow{20^\circ} Mo(CO)_3\cdot(IX)_2\ ; \\ \xrightarrow{80^\circ} Mo_2(CO)_3\cdot(IX)_4\ . \end{cases}$$

The structure of the dinuclear complex was demonstrated by X-ray diffraction. The difference in the ligand environment of the molybdenum atoms and the presence of a direct bond between them are noteworthy. Both these factors are not characteristic of the dinuclear complex obtained from the ligand (X).[66]

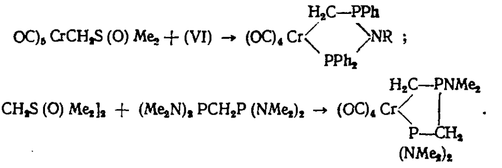
There are isolated mentions in the literature of the possibility of the hexa-ligand transfer reactions of the carbonyls of the metals considered. Thus, when the ligand (IX) is used under the conditions of photochemical stimulation, a spirotricyclic complex is readily formed.[92] Analogous substitution takes place with the tetrafluoride of *N*-phenyldiphosphorimidous acid (XIV).[93] A spirotricyclic complex of chromium has been obtained also on cocondensation of the metal vapour with the ligand (IX), while the monodentate mixed acid amides and fluorides give rise to symmetrical acyclic adducts under conditions of this reaction.[94,95] The cocondensation of chromium vapour with a mixture of ligands gives rise to a set of complexes of different ligand composition, from which the product $[(IX)_2.Cr(F_2PNMe)_2]$ has been isolated in a pure form.[95]

We shall now turn to studies on ligand transfer reactions in which derivatives of Group VI metals in the +1 or +2 oxidation states are used as starting materials. This possibility has been demonstrated in two investigations:[62,96]

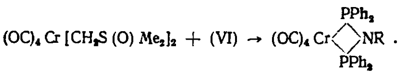


It is significant that the diastereoisomers are formed in unequal amounts; the ratio of the products depends on the type of the groups R and R′. Apparently this result is determined by an associative mechanism; in this case the transition states arising when the ligand attacks via two enantiomeric directions need not necessarily have the same energies.

There are also literature data on the ligand transfer reactions involving bidentate ligands. Thus one carbonyl ligand is displaced from a carbonyl of type (XV) on treatment with the tetrafluoride (IX).[97] It has been established very recently that the complexes of chromium carbonyl with the imides of diphenylphosphinous acid of type (VI) and the octamethyltetramide of methylenediphosphonous acid[98–100] form novel chromium-containing phosphaheterocycles:



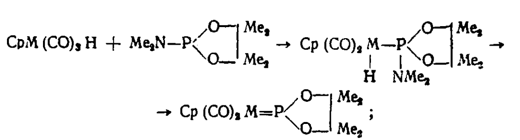
It has been concluded that the chromylide $(CO)_4Cr{=}CH_2$ is probably formed as an intermediate. However, this pathway is not obligatory:[99]



Systems in which the oxidation state of the metal is +2, namely cyclopentadienylmetal tricarbonyl chlorides,[97,101] readily interact with bidentate ligands of types (IX) and (XI) to form chelates. In the complex formation reaction in alcohol, the bidentate ligand (IX) can undergo alcoholysis:[97]

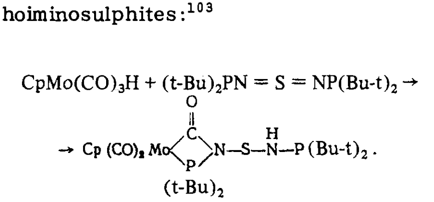
$$CpW(CO)_3Cl + (IX) + ROH \rightarrow CpW(CO)_2[PF(OR)_2]Cl.$$

We may mention specially the non-trivial reactions of hydride complexes. The following reactions have been discussed:[102]



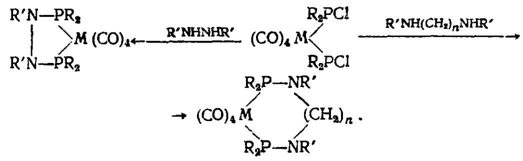
M=Cr, Mo, W.

The structure of compounds with a phosphorus–metal double bond had been demonstrated by X-ray diffraction. The phosphamide (I) enters into similar reactions. The hydrides considered react in an even more complex manner with phosphoiminosulphites:[103]

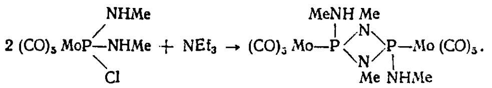


2,8-Dioxa-5-aza-1-phosphabicyclo[3.3.0]octane has been used as a ligand in complex formation reactions of neutral tungstates. It has been suggested that the overlap of the nitrogen and phosphorus orbitals is difficult in this compound for geometrical reasons, so that the phosphorus centre is less electron-donating, as a result of which tungsten is coordinated to the nitrogen atom. If the *P*-borate derivative is used in the complex formation reaction, then a stable *N*-tungsten adduct is formed.[104]

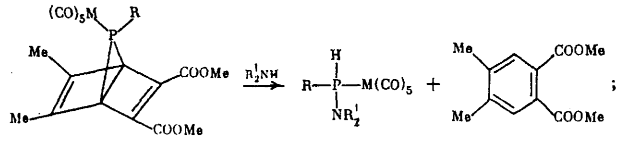
Combined synthesis of phosphamide complexes. Within the framework of this approach, the amido-group is introduced as a result of the substitution of the halogen atoms in halogenophosphine complexes. The simplest version of the synthesis consists in the interaction of monochlorophosphine systems with secondary amines.[105] More complex reactions involving secondary diamines and dialkylhydrazines can also be included here:[106]



The reaction of halogenophosphine complexes with ammonia and primary amines#,[77,107–110] including primary diamines,[106] with other functional groups[108,111] is widely used. We may mention specially the dehydrochlorination of chloramide complexes which can lead to dinuclear complexes inaccessible by other procedures, for example:[107]



The reactions of nitrogen-containing bases with halogenophosphine complexes proceed in an unusual manner in many instances. Thus the coordination compounds of molybdenum with CCl_3PF_2 phosphorylate very readily secondary amines via the P–CCl_3 bonds and not the P–F bonds.[112] The synthesis of hydrogen-containing aminophosphine complexes is chemically even more interesting:[113]



M = Cr, W; R = Ph, Me; R$'$ = H, Et, Ph.

The possible mechanisms of this reaction have been analysed.[113]

In the course of studies designed to demonstrate the structures of the complexes investigated using physicochemical methods, certain interesting rules have been established. Thus it has been shown that the direct coordinate bonds (^{97}Mo–^{31}P [114] and ^{183}W–^{31}P [51]) depend on the electronegativity of the atoms linked to the phosphorus atoms. In the ligand sequence obtained, phosphamides are located between phosphines and phosphites. Qualitatively the same picture can be traced in coordination shifts.[51] It is of interest that each type of complex (phosphine, phosphite, and phosphamide) constitutes a specific family when the direct coordinate bonds (^{183}W–^{31}P) are correlated with the ν(CO) frequencies in the IR spectra.[55]

(*c*) *Complexes of Group VII metals.* The general postulates which we have already mentioned in relation to the synthesis of Group VI metals hold also in relation to the synthesis of complexes of Group VII metals. One can only point to the smaller number of the relevant studies and the fact that they are almost all devoted solely to manganese derivatives. The principal method of synthesis of these compounds is the

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#The reactions can have specific pathways. In contrast to other primary amines, the interaction of t-$BuNH_2$ with the complex $(CO)_5MoPCl_3$ leads to the formation of a diphosphorus cyclic derivative and not a monophosphorus derivative.[77]

ligand transfer reaction. The dinuclear zero-valent manganese carbonyl complex $Mn_2(CO)_{10}$ has been used in reactions with the phosphamides (I) [115] and (VII).[36] The cyclic iron–arsenic–manganese cluster reacts with the ligand (I) via the dissociation of the manganese–iron bond.[116]

The readily available derivatives of metals in the +1 oxidation state of the type of $CpMn(CO)_3$ [57,117] and $Mn(CO)_5Br$ [41] have been most often used as the initial compounds. One and sometimes also two of their ligands are readily substituted by the simplest TPAA. More complex reactions have also been described, for example:[118]

$$CpMn(CO)_2THF + Ph_2PN{=}CMn(CO)_2Cp \rightarrow Cp(CO)_2Mn{-}PPh_2N{=}CMn(CO)_2Cp.$$

Interesting data have been obtained using tetraphenyldiazaphospholes.[119] The *trans*-isomer ensures the mono-ligand transfer reaction involving $Mn(CO)_5Br$. The *cis*-isomer is capable of double substitution to give *mer*-$Mn(CO)_3L_2Br$. If one begins with the corresponding rhenium derivative, then double substitution takes place with both ligands.

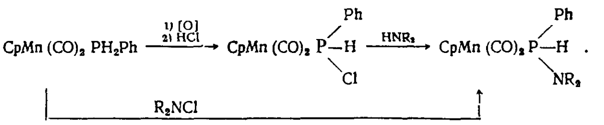
Bidentate ligands have also been used in a series of studies. Thus treatment of $Mn(CO)_5Br$ with the ligand (XI) results in the effective substitution of two carbonyl groups,[80] while in the interaction of $[Re(CO)_3(THF)_2Br]_2$ with 1,3-di-t-butyl-2,4-dimethyl-1,3,2,4-diazadiphosphetidine [120] two THF molecules are substituted. Similar processes also occur in the $CpMn(CO)_3$–ligand (IX) system.[97]§

TPAA with the α-pyridyl residue incorporated in the phosphamide fragment are also capable of single or double insertion in the coordination sphere as a result of the displacement of carbon monoxide.[76]

In the reactions described above coordination involved the phosphorus centre of the ligand. It has been shown[122] that, for the dinuclear complexes of rhenium, there is a possibility of the parallel *PN*-coordination when phosphineiminoamide ligands are used.

Derivatives of manganese in the +2 oxidation state have also been investigated in ligand transfer reactions.[57,123,124] Here we may mention the synthesis of diastereoisomeric components using optically active phosphamides.[123,124]

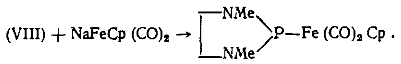
The synthesis of the phosphoramidite complexes of Group VII metals by the combined method has been little studied. Only one communication on this topic has been published:[125]



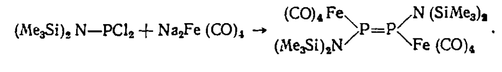
We may mention that the chlorophosphine derivative formed in the first stage is labile and rapidly disproportionates, while the corresponding phosphamide product is stable.

(d) *Complexes of Group VIII metals.* The greatest number of studies have been devoted to the synthesis of the phosphamide complexes of Group VIII metals. Bearing this in mind and also the known specific features of the individual families of elements of this Group, we have divided the entire data into sections in terms of three triads.

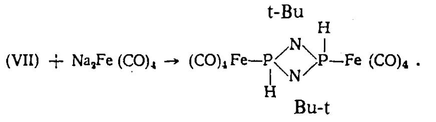
The metals of the first triad (Fe, Ru, Os) exhibit widely the 0, +1, and +2 oxidation states. The coordination systems in which we are interested have been obtained only by direct synthesis. Electrophilic substitution at the metal atom incorporated in the structure of the carbonylate anion has been used within the framework of this method, for example:[43]



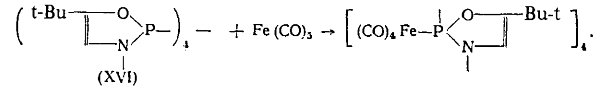
The employment of carbonylates with the more electron-donating iron atom in the interaction with the same acid fluoride (VIII) leads to the formation of a complex of the corresponding amide of hypodiphosphorus acid.[43] An even more complex compound has been obtained in the related reaction based on phosphoramidous chlorides:[48]



The author did not consider the chemistry of this process. An unusual derivative of the diamide of hypophosphorous acid has been obtained by treating the above carbonylate with the ligand (VII).[126] The traces of water present are apparently the source of hydrogen:



The ligand transfer reactions of the simplest complexes of the metals in the triad have been studied in greater detail on treatment with TPAA. In these reactions the TPAA usually do not lose any atoms or groups, as mentioned above. In individual experiments, such loss nevertheless occurs, but the structural element separated from the phosphorus remains part of the composition of the complex. We may mention the principal aspects of the investigations. The phosphamide (I) [127] and monoaminophosphines[41,128] react with $Fe(CO)_5$ to form monosubstitution products. Apart from monodentate ligands, bidentate[129,130] and tetradentate[131] ligands have been used in the reactions with $Fe(CO)_5$. As an illustration, we may quote the reaction



It is significant that the initial tetramer (XVI) behaves differently in the complex formation reactions—in its reaction with boron trifluoride ether, it is converted into the monomeric form and gives rise to a boron complex of a derivative of dicoordinate phosphorus, while in the example quoted only carbon monoxide is displaced from the four $Fe(CO)_5$ molecules. The structure of the iron complex has been demonstrated by X-ray diffraction and a significant difference between the lengths of the P—N bonds has been demonstrated (the distance is 1.737 Å for the bonds involved in both the small and the large rings, while the distance is 1.676 Å for the bonds in the large ring only). This difference is apparently determined by the different interactions of the unshared electron pairs of the nitrogen atoms with the electrons of the two phosphorus–iron coordinate bonds conjugated with them.

Phosphoramidous halides have also been introduced into the ligand transfer reaction.[132–134] If Lewis acids are added to the reaction mixture, then the primary adduct can ionise. In the synthesis of complexes of the type $Fe(CO)_4L$, one may begin with cluster carbonyls whereupon structurally simpler iron carbonyls are usually formed as side products (they sometimes also undergo ligand transfer reactions).[19,53,75,93,]

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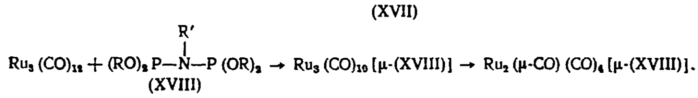
§ The carbene complexes of manganese behave analogously.[121]

[132,135–137] It has been suggested that complexes of zero-valent iron with TPAA be synthesised also by the cocondensation of the metal vapour with monodentate[95] and bidentate[95,138] ligands. The iron atoms in these compounds are linked to five phosphorus atoms having identical or different substituents.

The coordination compounds of TPAA with zero-valent ruthenium and osmium have been little studied. The following methods of their synthesis have been described in the literature:[139–141]

$$\mathrm{RuH(O_2CMe)(PPh_3)_3} + \underset{\text{(XVII)}}{\mathrm{F_2PNMe_2}} \rightarrow \mathrm{Ru\cdot(XVII)_5};$$

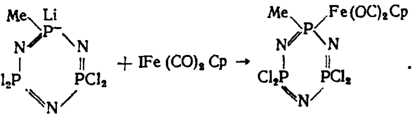


$$\mathrm{Ru_3(CO)_{12}} + \underset{\text{(XVIII)}}{\mathrm{(RO)_2P{-}\overset{\overset{\large R'}{|}}{N}{-}P(OR)_2}} \rightarrow \mathrm{Ru_3(CO)_{10}[\mu\text{-}(XVIII)]} \rightarrow \mathrm{Ru_2(\mu\text{-}CO)(CO)_4[\mu\text{-}(XVIII)]}.$$

The reactions of $Os(CO)_{11}(NCMe)$ and $H_2Os(CO)_{10}$ with the phosphoiminosulphite $(t\text{-}Bu_2PN)_2S$ have been carried out for osmium.[142]

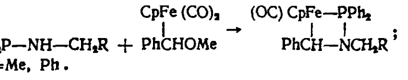
The coordination compounds of iron and the +1 oxidation state having phosphamide ligands have been studied non-systematically. The possibility of the exchange of carbon monoxide for an optically active phosphamide in the prochiral allylnitrosodicarbonyliron complex has been reported.[143] The reaction resulted in the formation of a mixture of two diastereoisomers, which was resolved by the usual procedures.

The synthesis of complexes in the molecules of which the central atom is in the +2 oxidation state has been studied relatively widely. The preparation of coordination compounds by nucleophilic substitution at the metal atom has been described:[144]



The mode of coordination and other related questions have been analysed using X-ray diffraction data. In addition, the usual ligand transfer reactions of carbonylcyclopentadienyliron derivatives, accompanied by the displacement of one or two carbon monoxide molecules on treatment with phosphorous triamide[127] or phosphoramidous fluorides,[57,97] the tetrafluorides of diphosphorimidous acids,[97] and phosphinous acid amides[145–147] have been used in a series of studies. Among the reagents mentioned, optically active substances have been frequently used, which made it possible to obtain systems with a chiral iron atom. The possible epimerisation and migration of the carbonyl in these derivatives has been discussed in a number of studies.[145,147,148]

If the ligand transfer reaction is carried out in its photochemical version, then other profound changes in the system are possible together with the exchange processes, for example:



$$\mathrm{Ph_2P{-}NH{-}CH_2R} + \underset{\mathrm{PhCHOMe}}{\overset{\mathrm{CpFe(CO)_2}}{|}} \rightarrow \underset{\mathrm{PhCH{-}NCH_2R}}{\overset{\mathrm{(OC)CpFe{-}PPh_2}}{|\quad\ \ |}};$$
$$\mathrm{R{=}Me,\ Ph.}$$

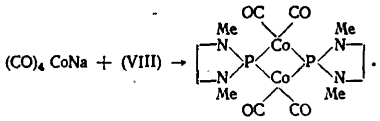
When R = Ph, the iminophosphine complex is obtained.[149]

Ruthenium complexes of the phosphoramidous difluoride (XVII) are readily formed from chlorides stabilised by triphenylphosphine. In the course of the synthesis triphenylphosphine is partly displaced:[150,151]

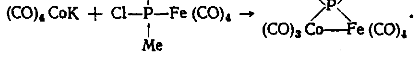
$$\mathrm{RuCl_2(PPh_3)_3} + \mathrm{(XVII)} \rightarrow \mathrm{RuCl_2(PPh_3)_2(XVII)_2}.$$

The adducts with different TPAA based on the chloroarene-ruthenium derivatives[152–154] as well as the corresponding hydrides[155] have been obtained analogously.

The Co, Rh, Ir triad. It has been suggested that electrophilic substitution at the metal atom be used to obtain the cobalt complexes. The carbonylate anions are usually made to react with phosphoramidous halides for this purpose, for example:[156]



Above we considered the analogous reactions of phosphorodiamidous fluoride (VIII) with iron and other transition metal carbonylates and noted that they all lead to mononuclear complexes. It is of interest that the phosphonamidous chloride derivative of iron tetracarbonyl gives rise to a heterometallic complex on interaction with cobalt carbonylate:[137]



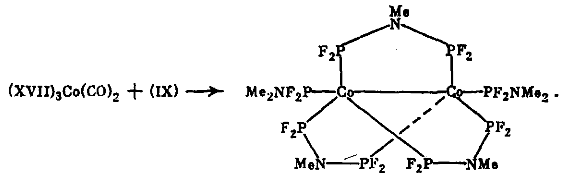
Dinuclear carbonyls, for example $Co_2(CO)_8$ (XIX), can also be involved in the cyclic cluster formation reaction.[157] The cluster obtained proved to be an extremely promising initial compound for the synthesis of other skeletal systems.[158,159]

Together with the electrophilic substitution method, the ligand transfer method has also been used to synthesise cobalt complexes of TPAA, for example:[41,127]

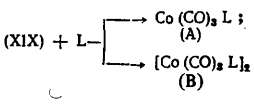
$$\mathrm{CpCo(CO)_2} + \underset{\text{(XX)}}{\mathrm{Me_2PNMe_2}} \rightarrow \mathrm{CpCo(CO)(Me_2PNMe_2)};$$
$$\mathrm{Hg[Co(CO)_4]_2} + \mathrm{(I)} \rightarrow \mathrm{Hg[Co(CO)_3\cdot(I)]_2}.$$

Ligand transfer reactions of this type with structurally similar cobalt complexes $Cp(CO)_2Co(R_F)I$, whose molecules contain the metal atom in the +3 oxidation state, have been achieved using optically active phosphinous amides. Two diastereoisomers are formed in this instance, their ratio being determined by the perfluoroalkyl group R_F.[160]

A relatively complex instance of the ligand transfer reaction makes it possible to obtain a dinuclear complex in a photochemical experiment from a phorphorus-containing mononuclear complex and the ligand (IX):[161]



Cobalt octacarbonyl (XIX) has been studied more widely in the ligand transfer and accompanying reactions. It has been stated that this compound reacts with the ligands (XX) [41] and (I) [127] to give ionic products. The structure of the compounds has not been demonstrated in detail. Subsequently this reaction was investigated in another study[78] where the formation of paramgnetic mononuclear products (A) was established for the full amides of phosphorous acids, while dinuclear diamagnetic substances (B) were found to be produced in the reactions involving the phosphoramidous esters (cyclic and linear):



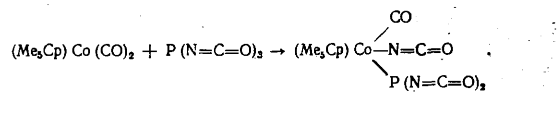
$$\mathrm{(XIX)} + \mathrm{L} \begin{cases} \rightarrow \underset{\text{(A)}}{\mathrm{Co(CO)_3L}}; \\ \rightarrow \underset{\text{(B)}}{\mathrm{[Co(CO)_3L]_2}}. \end{cases}$$

The octacarbonyl (XIX) has been studied in detail in the reaction with the bidentate ligand (IX). The reaction at 20 °C leads to the formation of the dinuclear dicarbonyl $[Co_2(CO)_2(IX)_3]$.¶ On photochemical activation and when an excess of the ligand is used, the product of the full ligand transfer reaction $[Co_2(IX)_5]$ is obtained.[162] There are three chelating ligands in the molecules of each of these complexes, which give rise to five-membered rings with two cobalt atoms. A similar result has been noted also in the reaction of the octacarbonyl (XIX) with the phosphoimine (XIV).[93] Dinuclear systems have also been obtained by the cocondensation of cobalt vapour with the corresponding ligands.[95,161]

The synthesis of cationic cobalt phosphamide complexes by the reaction of cobalt(II) perchlorate with the bidentate ligand $(Ph_2P)_2NPh$ has been reported.[163] Analogous cobalt compounds with α-diphenylphosphamidopyridine have been described.[6] The reactions leading to cobalt–aluminium complexes are chemically more involved:[164]

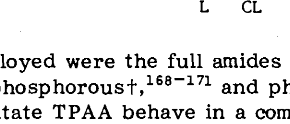
$$CoCl_2[P(NR_2)_3]_2 + AlCl_3 + P(NR_2)_3 \rightarrow CoCl[P(NR_2)_3]_3[AlCl_4].$$

The oxidative addition of the triisocyanate of phosphorous acid to the simplest cobalt complexes merit special attention:[165]



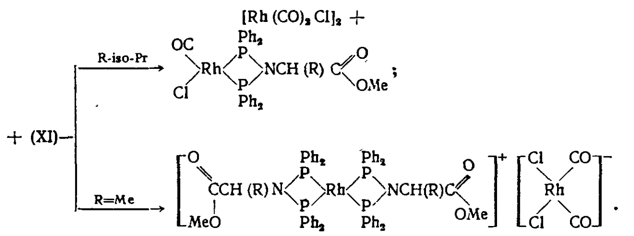
$$(Me_5Cp)Co(CO)_2 + P(N{=}C{=}O)_3 \rightarrow (Me_5Cp)Co(CO)(N{=}C{=}O)(P(N{=}C{=}O)_2).$$

Particularly numerous studies have been devoted to the rhodium complexes of TPAA, which can be accounted for by their catalytic activity. The latter factor affects also the character of the investigations carried out: the published articles frequently describe not individual coordination compounds but compositions comprising them, which are designed for catalysis (such compositions were examined in the Section devoted to catalysis). In contrast to cobalt complexes, the above compounds are more homogeneous in terms of the principal chemical features. As a rule, the central atom of the molecule is in the +1 oxidation state. The methods of synthesis of these systems are also relatively similar. They usually consist in the interaction of carbonyl or olefinic dinuclear complexes with TPAA and the process involves either the substitution of the ligand or the breaking of the $[\mu\text{-}X_2]$ bridges. We shall consider the latter possibility. In many studies the formation of the *trans*-complexes from μ-dichlorotetracarbonyldirhodium has been investigated:



$$[Rh(CO)_2Cl]_2 + 4L \rightarrow Rh(OC)(L)(L)(Cl).$$

The ligands employed were the full amides of phosphorous,[166 167] alkyl phosphorous†,[168–171] and phosphinous[23,172] acids. The bidentate TPAA behave in a complex manner. The cyclodiphosphazan (VII) and the corresponding difluoride give rise to different types of complexes depending on the reactant ratio.[36,173] The ligand (XI) and its analogues ensure the chelation of the metal:[80,81]



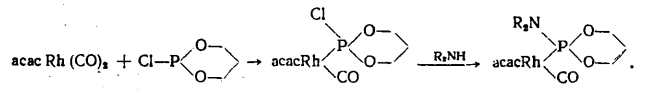
This example demonstrates the detailed influence of structural factors on the course of the complex formation reaction. It has been shown in a number of studies that the interaction of μ-dichlorotetracarbonyldirhodium can lead to not only the mononuclear complexes already examined but also to dinuclear complexes.[166,171,173] According to Nifant'ev et al.[171] such a process involving monodentate phosphamides takes place when the reaction is carried out in the presence of oxygen.

Bidentate ligands make it possible to obtain dinuclear rhodium complexes more frequently than the monodentate ligands. A dinuclear complex with a ruptured chlorine bridge has been obtained from the hard ligand (X),[67] while a complex with the intact bridge has been obtained from the relatively labile imide of diphenylphosphinous acid.[174,175] A result close to the latter case has been obtained in a study with the ethylimides of dimethyl-[176] and diphenyl-phosphorous acids (XVIII),[177] although here too the influence of the ester group on the details of the structure of the dinuclear complexes was manifested.

We shall consider the ligand transfer reactions of olefinic π-complexes of rhodium(I) chloride. These substances can be converted into mono- and di-nuclear coordination systems. Thus, according to the data of Aresta et al.[178], the ethylene π-complex and the phosphamide (I) react at 20 °C to form a product resulting from the rupture of the chlorine bridge. In other studies[179,180] dinuclear complexes were synthesised. Phosphoramidous fluorides of type (XVII) have been introduced into the ligand transfer reaction; the possibility of the complete substitution of the ethylene ligand by phosphamide ligands was demonstrated.[181]

Cyclo-octadiene derivatives of rhodium(I) chloride react with bidentate ligands of type (VII) to form dinuclear complexes in the molecules of which the metal atoms are coordinated to different phosphorus atoms.[82] Extensive, including complete, substitution of primary ligands by the bidentate ligands occurs upon the addition of tetrafluoroborates.[22]

The readily available acetylacetonatodicarbonylrhodium, which readily reacts with a wide variety of 2-amino-1,3,2-dioxaphosphorinanes [183] and 2-amino-1,3,2-oxazaphosphorinanes,[184] can be used for the synthesis of stable mononuclear complexes of univalent rhodium with one phosphamide ligand. The axial orientation of the metal relative to the six-membered ring of the ligand has been established in the complexes obtained. Some of the phosphamide complexes of the type considered have been synthesised in accordance with a two-stage scheme:[183]



On interaction with phosphamide in the presence of perchloric acid, the acetylacetonatorhodium(I) derivative with the cyclo-octadiene ligand exchanges the acetylacetonato-group and not the olefin group.[185]

¶The ligand transfer reaction of cobalt dodecacarbonyl has also been described briefly in the literature.[93]

†The results of the study of Grishina et al.[170] have been partly revised.[171]

In conclusion of the consideration of the synthesis of rhodium coordination compounds, we shall deal with the interconversions of the phosphorus-containing complexes. The partial displacement of PF_3 from the coordination sphere on treatment with the ligand (I) has been reported.[167] The reduction of phosphamide complexes of rhodium(I) is also of great interest.[186,187]

The synthesis of coordination compounds of iridium with TPAA has been little studied.

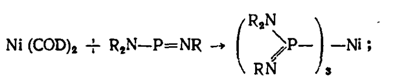
Complexes with the bidentate ligand (VI), obtained from the cyclooctadiene (COD) derivatives of iridium, have been reported:[188]

$$[Ir(COD)Cl]_2 + (VI) \rightarrow [Ir\cdot(VI)_2]Cl\,.$$

The reaction of the complex $[Ir(C_8H_{14})_2Cl]_2$ with an excess of PF_2NMe_2 leads to the formation of the complex $IrCl.\,.(PF_2NMe_2)_3$, in which there are no intermolecular Ir–Ir contacts, in contrast to the PF_3 derivatives.[189]

The Ni, Pd, and Pt triad. The study of the synthesis of complexes of the metals of the last triad with TPAA has its characteristic features. Thus, the relevant derivatives of all the elements of this family have been investigated to approximately the same extent. The second feature is manifested in the relative chemical paucity of the field considered. Thus there are virtually no reactions involving the formation and decomposition of clusters on complex formation, there are almost no unexpected reactions, and the syntheses in the coordination sphere of the metal have been little developed.

We shall consider the formation of phosphamide complexes of zero-valent metals. A series of studies on the ligand transfer reactions of $Ni(CO)_4$ have been published. The process involving the monodentate ligands (I),[2,5,127,190] (V),[75] and (XX),[41] phosphoramidous halides,[2,191] and the complex cyclic phosphamides $P_4(NMe)_6$ [192] and $MeP[N(R)SiMe_2]_2$ [193] is accompanied by the substitution of one or two carbonyl groups. The reaction with the bidentate ligand (IX) can be more far reaching and may even involve complete substitution.[130] The silylated amidoimide complex of zero-valent nickel (XXI) has been synthesised with the aid of the ligand transfer method:[194]



$$Ni(COD)_2 + R_2N{-}P{=}NR \rightarrow \left(\begin{matrix}R_2N\\ \quad\;\rangle P{-}\\ RN\end{matrix}\right)_3{-}Ni\,;$$

$R{=}SiMe_3$.

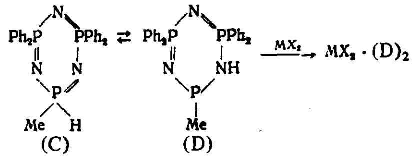
(XXI)

Nickel complexes containing only phosphamide ligands have also been obtained from the metal vapour.[95]

Coordination compounds of platinum have been studied in greatest detail by Scherer, who showed that biscyclooctadieneplatinum reacts with amidoimides of type (III) to form substances having the composition $Pt(III)_3$.[195] The interaction of the ligand (III) with cyclic platinum clusters has also been achieved:[196]

$$Pt_3(\mu\text{-}CNR)_3(CNR)_3 + (III) \rightarrow Pt_3(\mu\text{-}CNR)(CNR)_3\cdot(III)_2\,.$$

The preparation of complexes of bivalent metals has been described fairly extensively. Nickel, palladium, and platinum salts or their benzonitrile and similar derivatives form complexes effectively with various full amides[1,5,75,78,197,198] and amidoesters[104,199–202] of tervalent phosphorus acids and the amidoimides (III).[202] The reaction of acetonitrile solutions of palladium and platinum halides with an unusual cyclotriphosphazene is of special interest:[203]



According to ^{31}P NMR data, the initial phosphazene exists almost fully in the form (C), which, however, being a prototropic system can be converted into the form (D) to form a complex.

The study of the interaction of triethylphosphine derivatives of platinum and palladium dichlorides with di- and triazaphospholes established that the primary adducts can have different compositions. It has been suggested that the ligand is coordinated with both phosphorus and nitrogen atoms.[204]

Bivalent metal salts have been made to react with bidentate ligands (VII),[205] (XI),[80,81] (VI),[85] and (XVIII) [71] and mononuclear, including chelate, and dinuclear complexes were obtained. Nickelocene, π-allylpalladium chloride, Zeise's salt, and other similar organometallic compounds have been widely investigated in reactions with TPAA. The full amides[206,207] and amidoesters[202,208,209] of phosphorus acid, including those containing carbohydrate residues in their molecules,[168,210] as well as the bidentate ligands (VII) [211] and (VI) [212] have been resorted to as the latter.

In conclusion we shall deal with the intracoordination synthesis of phosphamide complexes. Phosphatrihalogeno-,[197,213–215] phosphamidohalogeno-,[216] and phosphinohalogeno-derivatives[80,214,217] of metals react satisfactorily with amines, being converted into the required complexes. Unfortunately the reaction is not of general importance.[213,214] Metal amides are phosphorylated more effectively than amines.[214,215]

III. CHEMICAL PROPERTIES

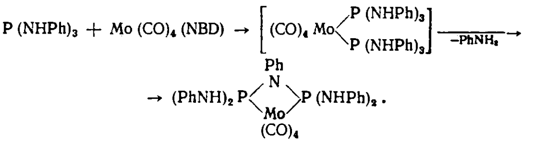
The publications on this question are divided into three groups. The first, main group includes studies on reactions involving the phosphamide (phosphimide) fragment of the ligand without affecting the coordination sphere. The data obtained are important for the synthesis of new types of phosphorus-containing complexes. At the same time they are of fundamental significance in a general chemical sense, because they demonstrate the influence of the metal on the reactivity of coordinated organophosphorus systems. The second group includes studies devoted to the preparation of complex organic compounds, the phosphorus-containing and metallic components of the complexes fulfilling only auxiliary functions. Studies on the last group are concentrated on the inorganic aspect of the chemistry of complexes—oxidation-reduction processes, additional complex formation via the functional groups in the side chains, and ligand transfer reactions.

1. The Reactions of the Coordinated Ligand Via the Phosphamide (Phosphimide) Bond

In the first place we shall consider the reactions of complexes involving a single P–N bond. TPAA are known to be labile and to undergo readily reactions via the phosphamide functional group on treatment with reagents whose molecules contain a mobile hydrogen atom or a polar double bond.[218] The possibility of involving also metallic complexes of TPAA in similar reactions has been discussed in a series of studies in recent years. It has been established that their P–N bond is cleaved by hydrogen chloride with formation of phosphochloro-[41,59,62,113,117,135,136,219,220] or amidophosphochloro-complexes.[107,137]# In many cases hydrochlorination is accompanied by profound skeletal rearrangements.[91] Overall, the hydrochlorination of the complexes proceeds readily, although it requires more severe conditions than the corresponding reactions of the free ligands.[136] The complexes synthesised, which are as a rule difficult to obtain by other methods, are widely used for the preparation of a wide variety of types of phosphorus-containing coordination systems (see, for example, Refs.113, 137).

The phosphamide complexes also react with hydrogen bromide,[69,72,107,113,117,136,219] hydrogen iodide,[107,113,117,219] and hydrogen fluoride.[117,146] Instead of the last compound, it is sometimes convenient to use benzoyl fluoride.[117] The deamination reaction considered makes it possible to solve simply certain coordination-chemical problems; for example, it permits the synthesis of enantiomeric complexes with a chiral metal atom.[146]

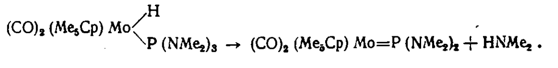
The hydrolysis[59,162] and alcoholysis[24,59,77,199] of the phosphamide complexes have been reported. The influence of the nature of the metal on the ease of the process has been established in relation to these reactions. Thus it has been shown that the copper complexes react more readily than the platinum complexes. In the latter case a positive effect is achieved only when acid catalysts are employed.[199] A characteristic reaction of the complexes, which has not been very widely investigated, is transamidation.[107] It leads to the disproportionation of the ligands:[221]



Thus the metal is a factor promoting the conversion of the trianilide of phosphorous acid into bis(phosphorodianilidato)-phenylamine and aniline. We may point out another possibility of inner-sphere phosphorylation:[222]

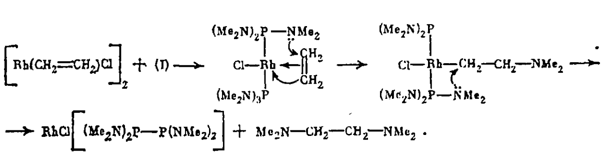
$$cis\text{-}\{(CO)_4Cr[(Ph_2P)_2NH]\} \xrightarrow[\text{2) } Ph_2PCl]{\text{1) BuLi}} cis\text{-}\{(CO)_4Cr[(Ph_2P)_3N]\}.$$

It is significant that this process is more effective than the analogous reaction without the participation of the metal. Phosphorylation accompanied by the formation of the P=M double bond is of great interest:

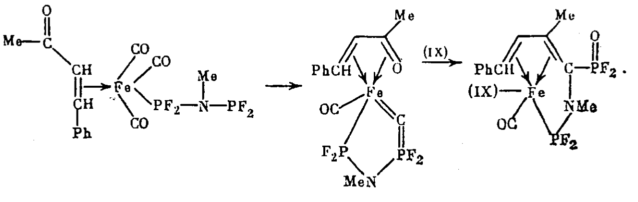


In the compounds obtained, sulphur, diazomethane, carbon disulphide, and iron carbonyls are inserted in this bond with formation of novel three- and four-membered cyclic derivatives.[102] The interaction of the phosphamide complexes with carbon dioxide, accompanied by the insertion of the reactant in the P–N bond, is no less important.[178]

The reaction of the phosphamide complexes with ethylene which has no analogy in the series of phosphamides, merits special attention:[178]

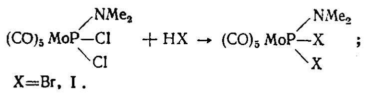


The reactions of benzylideneacetone, carbon monoxide, and the ligand (IX) coordinated jointly to the iron atom are formally similar to the above reaction:[129]



Individual motifs of this scheme can also be found in the paper of Newton and King.[223] On the basis of the data analysed, one may conclude that the possibilities of metal complex synthesis have begun to extend also to the synthesis of organic compounds which are difficult to obtain, including compounds which are extremely complex. Further development of this field of study is already urgently required. Success can be ensured only by a close cooperation between organophosphorus chemists and specialists in metal complex reactions.

The reactions of the coordinated phosphamide are not manifested solely by the degradation of the P–N bond. It is extremely significant that this structural unit can facilitate the substitution of other groups linked to the phosphorus atom. Thus the molybdenum complex with PCl_3 does not exchange chlorine atoms on treatment with hydrogen bromide and iodide. However, this reaction does occur with the corresponding phosphoramidous chloride complex:[107]

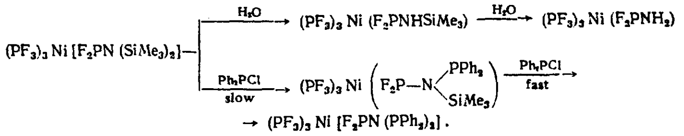


The amido-group probably exhibits a mesomeric electron-donating capacity in relation to the phosphorus atom, which promotes the heterolysis of the P–Cl bond.§ Nevertheless the unshared electron pair of the amido-group can ensure the formation of borate complexes[77] and protonation products. A stable ammonium compound has been detected only in a study involving a complex in which effective d_π, p_π-conjugation in the phosphamide fragment was not ensured for geometrical reasons.[220]

#For the description of the anomalous course of this reaction, see Müller and Vahrenkamp.[137]

§In relation to the hydrogen atom in the amidophosphohydride complexes, the amido-group exhibits electron-accepting properties. These complexes are readily deprotonated with formation of phosphorus-centred anions, which readily enter into reactions with electrophiles, forming various substances, including those which are virtually unobtainable in other ways.[224]

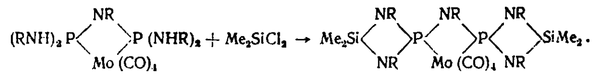
Among other reactions involving nitrogen, we may mention the desilylation of coordinated *N*-silylphosphamides:[214]



$$(PF_3)_3Ni[F_2PN(SiMe_3)_2] \xrightarrow{H_2O} (PF_3)_3Ni(F_2PNHSiMe_3) \xrightarrow{H_2O} (PF_3)_3Ni(F_2PNH_2)$$

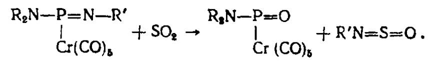
$$(PF_3)_3Ni[F_2PN(SiMe_3)_2] \xrightarrow[slow]{Ph_2PCl} (PF_3)_3Ni\left(F_2P{-}N\begin{matrix}PPh_2\\SiMe_3\end{matrix}\right) \xrightarrow[fast]{Ph_2PCl} (PF_3)_3Ni[F_2PN(PPh_2)_2].$$

Heterocyclic condensations are of interest,[106,110,222] for example:



The reactions of phosphimide complexes, i.e. systems with a P=N double bond, should be considered separately. These compounds are readily hydrated[202,225] and combine with alcohol,[202] forming the usual phosphamide coordination compounds. Certain complexes of Group VI metals with cyclic phosphimides readily undergo cyclo-oligomerisation.[74]

The deimidation of chromium complexes of the amidoimides of phosphorous acid is a reaction without analogy in the chemistry of classical organophosphorus compounds:[60]

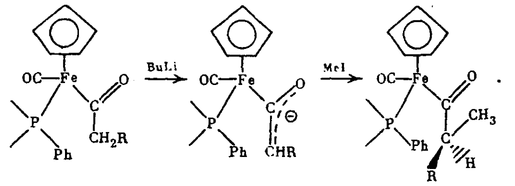


$$\underset{\displaystyle Cr(CO)_5}{R_2N{-}\overset{}{P}{=}N{-}R'} + SO_2 \rightarrow \underset{\displaystyle Cr(CO)_5}{R_2N{-}P{=}O} + R'N{=}S{=}O.$$

2. The Use of the Phosphamide Complexes in Fine Organic Synthesis

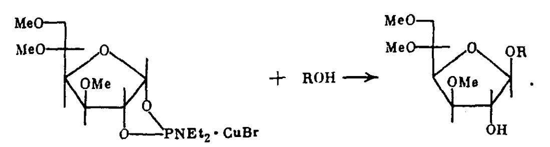
It has been shown[28] that the copper-lithium complexes stabilised by the hexaethyltriamide of phosphorous acid yield very satisfactory results in the specific α-alkylation of αβ-unsaturated ketones. The hydrolysis of the reaction mixture entails in this instance the complete decomposition of the complex and the decomposition of the ligand to water-soluble substances, which ensures the preparative employment of this important reaction.

The alkylation of Fe-acyl derivatives stabilised by phosphorus-containing ligands is of interest:[226]



It has been shown that the interaction of the O-anionic end of the ambident component of the side group with the benzene ring results in a definite diastereoselectivity. The most marked manifestation of this effect has been noted when phenylphosphamide ligands were employed.

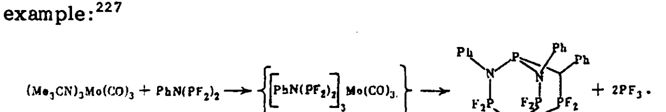
It has been suggested that the copper complexes of cyclic phosphoramidites (derivatives of carbohydrates) be used in glycosylation,[26] for example:



The cyclic phosphoramidites themselves behave in this reaction as phosphorylating agents. Thus complex formation involving the phosphorus atom alters significantly the nature of these derivatives.

3. Other Reactions

We shall consider the reactions involving the metal atom in the phosphamide complexes. The disproportionation of asymmetric ligands is sometimes observed. The disproportionation yields especially satisfactory results and the formation of highly symmetrical skeletal systems is possible, for example:[227]

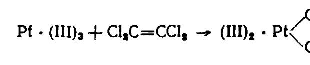


Another type of disproportionation has been described. It reduces to the redistribution of the ligands between individual molecules of the complex without altering their structure. As an illustration, we may mention the equilibrium established over a year at 20 °C:[191]

$$2Ni(CO)_2L_2 \rightleftarrows Ni(CO)_3L + Ni(CO)L_3\,;$$
$$L{=}Me_2NPF_2,\ EtNPF_2\,.$$

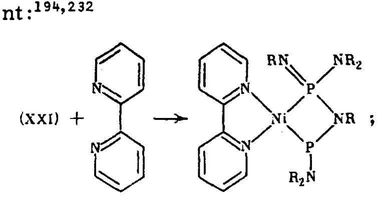
The displacement of one phosphamide ligand by another[228] or by P-ligands of a different chemical type[145,195] from the complexes has also been reported. Ligand transfer may be accompanied by profound changes in the structure of the coordination compound, for example, by the migration of the organophosphorus ligand from the metal to the π-bound benzene ring.[154]

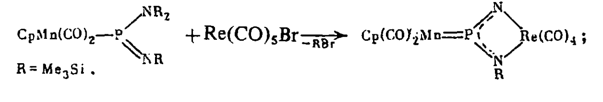
We shall now turn to reactions accompanied by a change in the oxidation state of the metal. The complexes may be reduced by chemical and electrochemical methods[15,115,229,230] and can be oxidised. The latter is especially interesting, because it can lead to structurally unusual results, for example:[225]



$$Pt\cdot(III)_3 + Cl_2C{=}CCl_2 \rightarrow (III)_2\cdot Pt\begin{matrix}CCl_2\\ | \\ CCl_2\end{matrix}.$$

In conclusion of this Section, we may point to the reactions of complexes having ligands with C–N groups in the side chains. These compounds can react with the simplest derivatives of metals, forming complex dinuclear systems.[231] The reactions of complexes whose ligands have P–N groups are even more interesting. In this case complex formation is accompanied by a far-reaching intracoordination rearrangement:[194,232]





IV. THE SEARCH FOR PRACTICAL APPLICATIONS

1. Catalysis

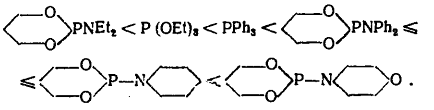
Functioning as ligands in metal complex catalysts, TPAA are in principle analogous to phosphines. Nevertheless, they are characterised by a wide variety of electronic and steric parameters to a greater extent in phosphines and other derivatives of tervalent phosphorus, which leads to very realistic prospects for the regulation of the activity and selectivity of catalytic systems. An important factor is also the availability of many TPAA.

Hydrogenation processes in the presence of complexes with phosphamide ligands have been studied in greatest detail. The first communications[233,234] on this question were devoted to the hydrogenation of styrene in the presence of the $[RhCl.(C_2H_4)_2]_2 + nL$ system. It has been established that the activity of the catalysts increases significantly on passing to phenylphosphamides whose molecules contain piperidine, pyrrolidine, or morpholine residues. The use of derivatives of less basic amines or amines with branched groups weakens sharply the catalytic properties. The general activity series summarised by James[235] are as follows:

$$PPhA_2,\ PPh_2A > PPh_3 > PA_3 \gg PAlk_3;$$
$$PPh_3 > PPh_2Alk \approx PAlk_2A > PPhAlk_2 > PAlk_3.$$

where A is the residue of the main and sterically unhindered secondary amine.

The influence of the nature of the ligands on the rate of hydrogenation has been observed in greater detail in a study[183] devoted to the acetylacetonate derivatives acacRh.(CO)L. The activity of the catalysts increases in the sequence



In many cases interesting results were obtained also with complexes having bidentate phosphamide ligands, for example, the ligand (XI).[80]

The substrate and the solvent[234,236] and also admixtures of oxygen play an important role in hydrogenation in the presence of various phosphamide complexes of rhodium. Oxygen oxidises the phosphamide ligands in mononuclear *trans*-complexes, which leads to the appearance of dinuclear complexes having a comparatively high catalytic activity.[171]

The use of optically active phosphamides to synthesise enantio-selective rhodium catalysts proved to be extremely fruitful. A wide variety of monodentate[237,238] and bidentate[239–248] ligands¶ were used for this purpose, the latter exhibiting the best activity overall. Optically active phosphoramidite complexes immobilised on mineral carriers have also been investigated, but their application does not yield appreciable advantages.[253]

The enantioselectivity of the phosphamide complexes and the configuration of the products of asymmetric hydrogenation probably depend on the nature of the amido-groups at the phosphorus atom.[240,245,254] Thus when the compounds $[Rh(CO)L]ClO_4$ are used in the hydrogenation of *N*-acylaminocinnamic acid, the transition from (1*R*, 2*R*)-bis(diphenylphosphinoamino)cyclohexane to (1*R*, 2*R*)-bis(diphenylphosphino-*N*-methylamino)cyclohexane leads to the inversion of the stereochemical result of the reaction.[254]

The use of palladium complexes with TPAA in hydrogenation is less well known. The full amides of phosphorous acid exhibited a high activity in the $C_3H_5PdLCl–NaBH_4–O_2$ system in the reduction of nitrobenzene, alkenes, and alkynes.[206,255] Systems obtained from phosphoramidites (derivatives of carbohydrates)[168,210,256] and cyclophosphorylated ephedrine[208,209] showed some catalytic activity. The possibility of using ruthenium complexes with the ligand (VII) in the hydrogenation of oct-1-ene has been indicated in the literature.[257]

The rhodium(I) complexes of TPAA yielded satisfactory results in the catalysis of hydroformylation.[172,258,259] The influence of the ligand on the direction of the process has been traced in relation to the hydroformylation of hex-1-ene. It has been shown that the increase of the π-acceptor capacity of the phosphoramidite, observed when aryl residues are introduced at the nitrogen atom, leads to an increase of the yield of the aldehyde having the normal structure. A decrease of π-acceptor capacity entails the formation of large amounts of the isomeric aldehyde. The use of polymeric complexes of the type $P–OC_6H_4NMePPh_2.RhCl(CO)$ has been reported.[172] It has been indicated that there is a possibility of the enantioselective hydroformylation of prochiral alkenes and of the hydrosilylation of ketones using rhodium complexes with optically active ligands.[249] The carboxylations of propene in the presence of a palladium catalyst, promoted by the full alkylamides of phosphorous acid, has also been described. The process selectivity reaches 79.5% with respect to isobutyric acid, which exceeds the selectivity of the catalytic system using PPh_3.[260]

We shall now turn to the catalysis of oligomerisation and polymerisation. A number of nickel and cobalt complexes containing the hexaalkyltriamides of phosphorous acid[164,261,262] and phosphamide bidentate ligands[163] are of technical interest for the polymerisation and oligomerisation of α-olefins and dienes. It is significant that nickel catalysts of this type can be used in an aqueous medium.[263] The oligomerisation of acetylenes in the presence of the $Pd(acac)_2.AlEt_3.L$ system has been investigated.[264] When $L = Ph_2PNMe_2$, the amount of dimer formed is smaller by a factor of two and the amount of higher oligomers is twice as great as in the case where $L = PPh_3$.

Among other possibilities of catalysis using the above complexes, we may point to the conversion of methanol into ethanol[89] and to the acceleration of diffusional photographic processes in sensitive layers of polymers.[265]

2. The Synthesis of Medicinal Drugs

Data on the synthesis of platinum complexes and positive results of their tests in the treatment of oncological affectations have been published.[1,200] Studies initiated at the present time are being extended to the field of complex biogenic systems.[199] It has been suggested that gold complexes based on azaphospholes be used in chrysotherapy.[33,204]

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Thus metal complexes of TPAA constitute a large class of coordination compounds which are constantly attracting increasing attention. An important feature of these systems is that their ligands are chemically varied. They are frequently extremely labile or do not exist at all as individual substances but are entirely stable in the coordinated state. Consequently the only source of any information about these phosphorous compounds is the study of their metal derivatives.

Complexes with TPAA enter into a wide variety of reactions in the coordination sphere of the metal. An important role is due in this instance to the phosphamide component of the molecule which either changes as a result of the dissociation of the P–N bond, or activates a neighbouring group, or

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¶ **Recently, particular attention has been devoted to ligands obtained by phosphorylating optically active aminoalcohols.**[249–252] influences the properties of the metal. In other words, the behaviour of the complex is not determined simply by the central ligand atom but also by the functional group based on it.

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Organotellurium Compounds in Organic Synthesis

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The review gives a systematic account of the survey of data on the application of organic compounds of tellurium in the synthesis of hydrocarbons, halogeno-derivatives, and carbonyl compounds.
The bibliography includes 94 references.

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I. INTRODUCTION

The chemistry of organotellurium compounds has developed extremely vigorously during the last 10–15 years. It is sufficient to point out that the number of studies published during these years exceeded the number of publications during the entire preceding 130 years of the development of organotellurium chemistry. The synthesis of organotellurium compounds, their reactivity, and their structures in the crystalline state and in solution have been considered in a number of monographs[1,2] and reviews.[3–11] As the chemistry of organic compounds of tellurium has developed, their applications in preparative organic chemistry for the synthesis of various classes of organic compounds have expanded vigorously, although in this respect tellurium compounds are so far inferior to organoselenium compounds.[12–14]

The wide variety of applications of tellurium compounds in organic synthesis is based on a number of their specific features, among which the following may be included: (1) the ease of converting tellurium(II) derivatives into tellurium(IV) derivatives and vice versa; (2) the high nucleophilicity of the RTe^- and Te^{2-} anions; (3) the much higher stability of derivatives of tetracoordinate tellurium (σ-telluranes) of the type $RTeX_3$, R_2TeX_2, and Ar_4Te compared with the analogous sulphur and selenium compounds; (4) the relative ease of eliminating the tellurium atom from tellurium(II) derivatives.

A series of new data on the application of organic derivatives of tellurium in the synthesis of a wide variety of organic compounds are described systematically and surveyed in the present review.

II. SYNTHESIS OF HYDROCARBONS

One of the most thoroughly investigated applications of organotellurium compounds in preparative organic chemistry involves their use for the preparation of hydrocarbons. This applies in the first place to unsaturated compounds and biaryls. The only reaction described hitherto in which organotellurium reactants have been used to synthesise benzene derivatives is based on the oxidation of arylhydrazines by di(p-methoxyphenyl)tellurium oxide,[15,16] leads to arenes in comparatively low yields, and can hardly be regarded as of preparative importance.

1. Saturatated Hydrocarbons

Saturated hydrocarbons are readily formed in 70–90% yields on reduction of organyltellurides (I) with triphenyltin tetrahydroborate in benzene at 20–80 °C [17] (judging from the analogous reaction with selenides,[17] $R^2TeSnPh_3$ is probably a side product):

$$\underset{(\mathrm{I})}{R^1TeR^2} \xrightarrow{Ph_3SnH} R^1H;$$

$$R^2{=}Me,\ R^1{=}C_{12}H_{25};\ R^2{=}Ph,\ R^1{=}C_{12}H_{25},\ C_8H_{19}CH_2CH(Me),$$
$$C_8H_{17}CH(OH)CH_2,\ C_8H_{17}CH(OCOMe)CH_2,\ Me(CH_2)_2CH(OH)\underset{|}{C}H(CH_2)_2Me.$$

The reduction does not involve functional groups such as OH, OCOR, and C=O, which makes it possible to obtain also the corresponding substituted derivatives in high yields.[17]

It is noteworthy that diorganyltellurium dichlorides are reduced more readily than tellurides, but the reason for this is not clear since tellurium dichlorides are reduced via the formation of tellurides:[17]

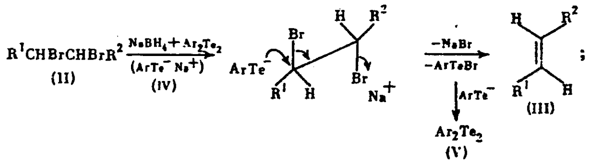
$$RTeCl_2Ph \xrightarrow{Ph_3SnH} RH;$$
$$R{=}C_{12}H_{25},\ C_8H_{19}CH_2CH(Me).$$

2. Olefins and Acetylenes

Various types of organotellurium compounds are used to obtain unsaturated compounds—olefins and acetylenes: derivatives of monocoordinate tellurium—tellurolate[18] and phosphorotellurolate anions;[19,20] derivatives of dicoordinate tellurium—diaryltellurides,[21,22] phenoxatellurin,[23,24] and diaryl ditellurides;[25] derivatives of tricoordinate tellurium—telluroxides,[12,26–29] and tellurium imides;[30,31] derivatives of tetracoordinate tellurium (σ-telluranes)—diaryltellurium dihalides[32] and organyltellurium trihalides.[32,33]

(a) *Catalytic Reactions with Particiation of Derivatives of Monocoordinate Tellurium*

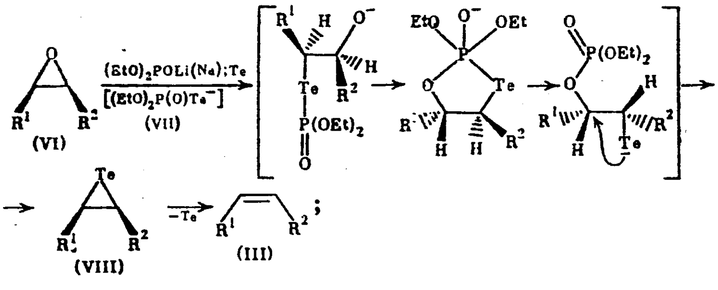
One of the most important and promising applications of organotellurium reagents in organic synthesis involves the possibility of using them under catalytic conditions. The application of diaryl ditellurides (V) [for di(2-thienyl) ditelluride as an example] as catalysts of the debromination of vicinal dibromides (II) in the presence of $NaBH_4$, which leads to the unsaturated compound (III) in high yields, may serve as a typical illustration:[18]



Ar = 2-thienyl; R^2 = Ph, Me, CO_2Et: R^1 = H, R^2 = C_8H_{17}; R^1 = Ph, R^2 = COOH; R^1 = R^2 = COOH; —$(CH_2)_6$—; (II) = 5α, 6β-dibromocholestan-3β-ol.

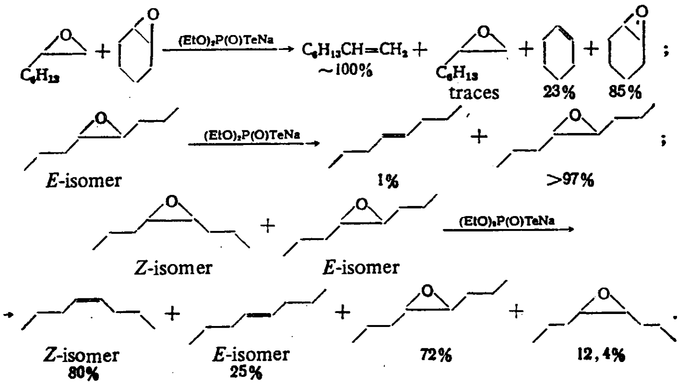
It has been suggested[18] that the main active species in this catalytic cycle is the tellurophenoxide anion (IV), formed on reduction of a diaryl ditelluride, whose halogenophilic attack on the bromine atom is accompanied by the anti-elimination of a second halogen atom with formation of the olefin (III). The course of this reaction (carried out in an atmosphere of nitrogen) is readily followed from the change in the colour of the solution from dark red (ditelluride) to colourless (tellurophenoxide anion).

Alkali metal *OO*-diethyl phosphorotellurolates (VII), among which the lithium derivative is the most active, are extremely effective reagents, which make it possible to convert the epoxides (VI) into olefins in high yields.[19,20] The deoxygenation of the epoxides as well as the dehalogenation of dibromides described above are carried out catalytically by adding tellurium (0.1–0.25 mmol) to a solution of diethyl phosphite (1–2 mmol) and epoxide (1 mmol).[19] The probable reaction mechanism includes the formation of unstable epitellurides (VIII):[20]



R^1 = C_6H_{13}, R^2 = H; R^1 = C_8H_{17}, R^2 = H; R^1 = $C_{18}H_{37}$, R^2 = H.

Compared with their selenium analogues, compounds (VII) are much more reactive and participate in catalytic deoxygenation reactions much more actively. Among epoxides, the terminal derivatives react most readily and among these the most reactive are the *Z*-isomers, which has been confirmed by the competing reactions shown below, with participation of the corresponding 1 : 1 mixtures of the epoxides. The deoxygenation with the aid of *OO*-diethyl phosphorotellurolates is stereospecific and *Z*- (or *E*-)epoxides always yield the *Z*- (or correspondingly *E*-)olefins:[20]



(b) Derivatives of Dicoordinate Tellurium

When a series of different diaryl tellurides (I, $R^1 = R^2 = Ar$) react with vicinal dibromides (II), the olefins (III) and diaryltellurium dihalides (IX) are obtained in high yields:[21]

$$\underset{(II)}{R^1CHXCHXR^2} + \underset{(I)}{Ar_2Te} \rightarrow R^1CH{=}CHR^2 + \underset{(IX)}{Ar_2TeX_2};$$

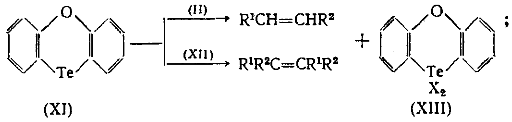
X=Br, Cl.

The reaction of diphenyl telluride (I, $R^1 = R^2 = Ph$) with 1,2-dibromoethane (II, $R^1 = R^2 = H$, X = Br) under mild conditions (refluxing for 30 min) affords a 74% yield of 1,2-bis(diphenyltelluronia)ethane dibromide (X), whose recrystallisation from glacial acetic acid produces diphenyltellurium dibromide (IX) and ethylene. The possibility of the intermediate formation of telluronium derivatives of type (IX) in reactions with participation of the substituted dibromides (II), arising in this connection, has not so far been investigated:

$$2Ph_2Te + CH_2BrCH_2Br \rightarrow \underset{(X)}{Ph_2\overset{+}{Te}CH_2CH_2\overset{+}{Te}Ph_2\ 2Br^-} \xrightarrow{AcOH,\Delta} \underset{(IX)}{Ph_2TeBr_2} + CH_2{=}CH_2.$$

Another dehalogenating agent in the series of derivatives of dicoordinate tellurium is phenoxatellurin (XI).[23,24] Its interaction with vicinal [compound (II)] and geminal [compounds (XII)] organic dichlorides and dibromides results in the formation of the corresponding olefins and 10,10-dihalogenophenoxatellurins (XIII) in high yields.

Presumably in the series of vicinal dibromides the reactions proceed via the intermediate formation of telluronium salts of type (X) and in the case of the geminal dibromides via carbenes:



(XI)
X=Cl, Br.

(XIII)

The reactions with participation of diaryl tellurides and phenoxatellurin are not, however, general, because the number of vicinal and geminal dihalides, such as 1,2-dichlorocyclohexane[23] and benzylidene chloride and bromide,[24] are not dehalogenated under the conditions indicated.

Phenoxatellurin is a more active dehalogenating agent than phenothiatellurin, which is in its turn superior to phenoxaselenin.[24] Phenoxatellurin is used also for the dehalogenation of unsaturated vicinal di-iodides, which makes it possible to obtain the corresponding acetylenes in high yields:[23]

$$PhCX{=}CXR + (XI) \rightarrow PhC{\equiv}CR + (XIII);$$

X=I, R=H (80%), COOH (87%).

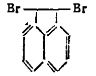
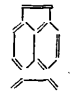
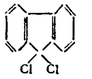
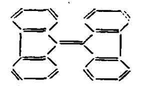
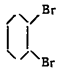
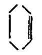
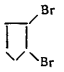
Together with diaryl tellurides and phenoxatellurin, diaryl ditellurides (V) are also used as dehalogenating agents.[25] The interaction of these compounds with the dibromide (II) is accompanied by the elimination of elemental tellurium with formation of the olefins (III) and the symmetrical diaryl tellurium dibromides (IX).

The possible ways of obtaining unsaturated compounds via the dehalogenation of vicinal and geminal dihalides by various organic derivatives of tellurium (II) are presented in the Table.

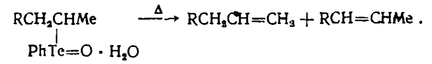
(c) Derivatives of Tricoordinate Tellurium

Telluroxides. Like selenoxides[12–14] telluroxides are now beginning to be used in the synthesis of olefins having different structures.[12,26–29] The possibility of employing telluroxides for the preparation of olefins was first investigated by Sharpless et al.[12] When alkyl phenyl tellurides were oxidised by t-butyl hydroperoxide in benzene, a mixture of olefins, probably formed via the *syn*-elimination of the intermediate telluroxides, was obtained in a low yield.[12]

The synthesis of olefins from diorganyl dihalides and organic derivatives of tellurium(II).

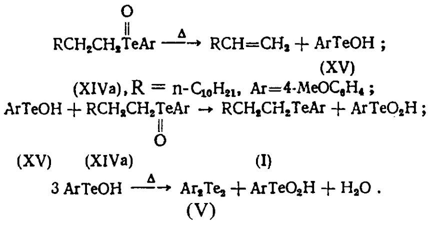
Dihalides (III) and (XII)			Te(II) derivative	Olefin	Yield, %	Refs.
R^1	R^2	X				
(III), Ph	H	Br	(XI)	$PhCH{=}CH_2$	77	[23]
(III), Ph	Ph	Br	Ph_2Te	PhCH = CHPh-*trans*	94	[21]
(III), Ph	Ph	Br	$(p\text{-}MeOC_6H_4)_2Te_2$	PhCH = CHPh-*trans*	90	[25]
(III), Ph	Ph	Br	$(p\text{-}EtOC_6H_4)_2Te_2$	$PhCH{=}CHPh$	100	[25]
(III), Ph	COOH	Br	Ph_2Te	$PhCH{=}CHCOOH$	100	[21]
(III), Ph	COOH	Br	(XI)	$PhCH{=}CHCOOH$	93	[23]
(III), Ph	COOH	Br	$(p\text{-}MeOC_6H_4)_2Te_2$	PhCH = CHCOOH-*trans*	68	[25]
(III), Ph	COOH	Br	$(p\text{-}EtOC_6H_4)_2Te_2$	$PhCH{=}CHCOOH$	85	[25]
(III), Ph	COOEt	Br	(XI)	$PhCH{=}CHCOOEt$	89	[23]
(III), COOH	COOH	Br	$(p\text{-}MeOC_6H_4)_2Te_2$	HOOCCH = CHCOOH-*trans*	73	[25]
(III), COOH	COOH	Br	$(p\text{-}EtOC_6H_4)_2Te_2$	HOOCCH = CHCOOH-*trans*	86	[25]
(III), Me	COOH	Br	(XI)	$MeCH{=}CHCOOH$	75	[23]
(XII), Ph	Ph	Cl	(XI)	$Ph_2C{=}CPh_2$	73	[24]
(XII), COOEt	COOEt	Br	(XI)	$(EtOOC)_2C{=}C(COOEt)_2$	52	[24]
			(XI)		23	[25]
			(XI)		97	[24]
			(XI)		62	[25]
			(XI)		83	[25]
Dibromocholesterol			Ph_2Te	Cholesterol	93	[21]

Subsequent studies[26–29] showed that the thermal decomposition of telluroxides can be used for the synthesis of olefins of different structures and compositions. The conditions in the thermolysis of telluroxides are determined by the structure of the alkyl group. Alkyl phenyl telluroxides (XIV), containing secondary alkyl groups, rapidly decompose at room temperature with formation of a mixtures of olefins in high yields.[29] Thus s-octyl phenyl telluroxides (XIV, $R = C_5H_{11}$) gives rise on decomposition to a mixture of oct-1-ene and *cis*- and *trans*-oct-2-enes in 80% yield together with a small amount of 2-octanol and 2-octanone. Telluroxides containing s-alkyl groups, such as 2-dodecyl, 2-tetradecyl, cycloheptyl, cyclo-octyl, and cyclododecyl, combined with other alkyl groups behave analogously.[29] On the other hand, cyclohexyl phenyl telluroxide (XVI) is extremely stable and decomposes only at 200–290 °C with formation of cyclohexane in a yield exceeding 70%;[29] however the causes of the increased resistance of this telluroxide to heating are not clear.


(XIV)

$$\underset{\underset{PhTe=O\cdot H_2O}{|}}{RCH_2CHMe} \xrightarrow{\Delta} RCH_2CH{=}CH_2 + RCH{=}CHMe\,.$$

In contrast to telluroxides with s-alkyl groups, those containing primary alkyl groups [compound (XIVa)] decompose under more severe conditions.[26,29] Thus n-dodecyl phenyl telluroxide (XIVa, $R = C_{10}H_{21}$, Ar = Ph) is cleaved with formation of dodec-1-ene (50%) at 1-dodecanol (11%)[29] at 200–240 °C, while n-dodecyl 4-methoxyphenyl telluroxide (XIVa, $R = n\text{-}C_{10}H_{21}$, $Ar = 4\text{-}MeOC_6H_4$) affords a mixture of dodec-1-ene and the telluride (I) in proporations of 1 : 1 and 1.4 : 1 after refluxing for 24 h in CCl_4 or 12 h in toluene respectively.[26] The authors[26,29] believe that the primary intermediate in the decomposition reaction of telluroxide is tellurinic acid (XV), which reduces half of the telluroxide (XIV) to the telluride (I) in the next stage of the process. At the same time there is also a possibility of the disproportionation of this acid at a high temperature leading to the diaryl ditelluride (V):[26]



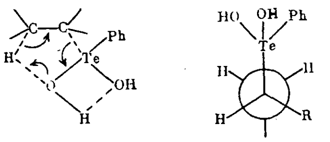
$$RCH_2CH_2\overset{\overset{O}{\|}}{Te}Ar \xrightarrow{\Delta} RCH{=}CH_2 + \underset{(XV)}{ArTeOH}\,;$$

$$(XIVa), R = n\text{-}C_{10}H_{21},\ Ar{=}4\text{-}MeOC_6H_4\,;$$

$$\underset{(XV)}{ArTeOH} + \underset{(XIVa)}{RCH_2CH_2\underset{\underset{O}{\|}}{Te}Ar} \rightarrow \underset{(I)}{RCH_2CH_2TeAr} + ArTeO_2H\,;$$

$$3\,ArTeOH \xrightarrow{\Delta} \underset{(V)}{Ar_2Te_2} + ArTeO_2H + H_2O\,.$$

It is believed[29] that the causes of the difference between the reactivities of telluroxides with primary [compounds (XIVa)] and secondary [compounds (XIV)] alkyl groups, which exist in the form of dihydroxytelluranes, are determined by the difference between the stabilities of the carbonium ions formed on cleavage of the C–Te bond (A) and also be the difference between the steric environments of these two types of telluroxides (B):

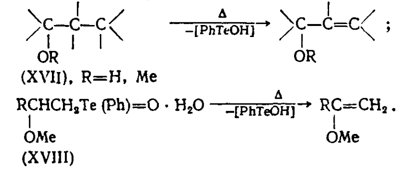


(A) (B)

(XIV), R = Alk: (XIVa), R = H.

In the case of telluroxides elimination takes place in such a way that terminal olefins are formed preferentially.[29] Thus the ratio of the mono- and di-substituted olefins [formed on decomposition of the telluroxides (XIV, $R = n\text{-}C_5H_{11}$ or $n\text{-}C_7H_{15}$], amounting to (2.48–2.50) : 1, is much higher than in the elimination reactions of the analogous selenoxides (1.56 : 1)[34] and sulphoxides (1.5 : 1).[35]

Like alkyl phenyl and cycloalkyl phenyl telluroxides, their analogues containing hydroxy- and methoxy-groups [compounds (XVII) and (XVIII)] are also capable of undergoing thermal decomposition; their decomposition leads to allyl alcohols and allyl and vinyl ethers in high yields:[27–29]



$$\overset{PhTe=O\cdot H_2O}{\overset{|}{\underset{\underset{OR}{|}}{>C}{-}C{-}C<}} \xrightarrow[-[PhTeOH]]{\Delta} \overset{|}{\underset{\underset{OR}{|}}{>C}{-}C{=}C<}\,;$$

(XVII), R=H, Me

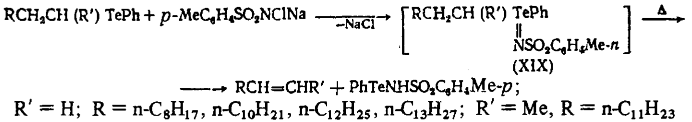
$$\underset{\underset{OMe}{|}}{RCHCH_2Te(Ph){=}O\cdot H_2O} \xrightarrow[-[PhTeOH]]{\Delta} \underset{\underset{OMe}{|}}{RC{=}CH_2}\,.$$

(XVIII)

Bearing in mind the relative ease of synthesis of alkyl phenyl telluroxides of the type of compounds (XIV) and (XVII)–(XVIII), there are good prospects that the reactions examined in this Section will be applied in organic synthesis.

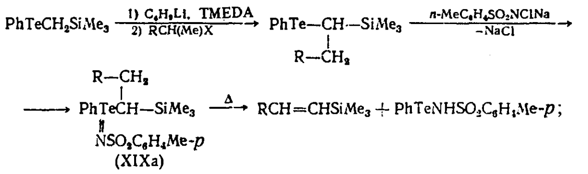
Tellurimides. It has been shown recently that olefins may be formed also on decomposition of tellurimides (XIX), which are believed tentatively to arise *in situ* on interaction of alkyl phenyl tellurides with an excess of chloramine T

(*N*-chloro-4-methyl-*N*-sodiobenzenesulphonamide) in boiling tetrahydrofuran (THF):[30]



$R' = H$; $R = n\text{-}C_8H_{17}$, $n\text{-}C_{10}H_{21}$, $n\text{-}C_{12}H_{25}$, $n\text{-}C_{13}H_{27}$; $R' = Me$, $R = n\text{-}C_{11}H_{23}$ (molar ratio $n\text{-}C_{12}H_{25}CH = CH_2/trans\text{-}n\text{-}C_{11}H_{23}CH = CHMe = 2.5 : 1.0$).

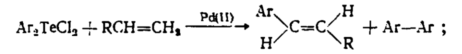
The tellurimides (XIXa), a scheme for the synthesis of which is presented below, afford fairly satisfactory yields of alkylvinylsilanes in the form of a 1 : 1 mixture of the *Z*- and *E*-isomers on pyrolysis *in situ* in boiling THF:[31]



$R = n\text{-}C_9H_{19}, n\text{-}C_{11}H_{23}, n\text{-}C_{13}H_{27}, n\text{-}C_{15}H_{31}$.

(*d*) *Arylation of Olefins*

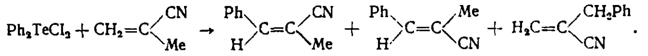
Like arylmercury chlorides[36,37] and arylthallium(III) derivatives[38] as well as the phenyl derivatives of magnesium (ArMgX),[39] Group IV elements (Ph_4Sn,[36] Ph_4Pb [36]), and Group V element (Ar_3P,[40] Ph_3As,[41,42] Ph_3Sb,[41,42] and Ph_3Bi [41,42]), the σ-telluranes Ar_2TeX_2 and $ArTeX_3$ [32] can be used to arylate olefins by carrying out the reaction in the presence of stoichiometric amounts of $PdCl_2$/MeCOONa. Mainly products with the *trans*-configuration (XX) together with small amounts of the biaryls (XXI) (1—6%) are then formed:[32]



(XX) (XXI)

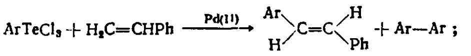
Ar=Ph, R=Ph, COOMe, CN, CHO, COMe, CH_2OCOMe; R=Ph, Ar=4-MeC_6H_4, 4-BrC_6H_4, 4-$MeOC_6H_4$.

The most varied olefins enter into the reaction: styrene, acrylic acid esters, acrylonitrile, methacrylonitrile, acroleine, methyl vinyl ketone, allyl alcohols, and allyl halides. In the reaction involving acrylonitrile, a 1 : 3 mixture of the *cis*- and *trans*-isomers was obtained while that of methacrylonitrile gave rise to a mixture of compounds (XX)—(XXIV) in proportions of 1 : 1 : 1.5:[32]



(XXII) (XXIII) (XXIV)

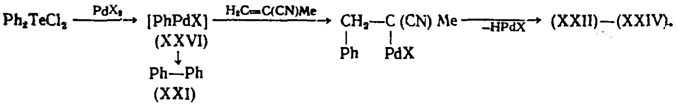
In the reactions of allyl alcohol and allyl bromide, the main products formed are β-phenylpropionaldehyde and allylbenzene respectively, as in the interaction of these compounds with phenylmercury derivatives.[37] The use of *p*-substituted diaryltellurium dihalides in this reaction leads (in the reaction involving styrene) to lower yields of *trans*-stilbenes than in the reaction with diphenyltellurium dichloride. The replacement of a chlorine atom by the acetoxy-group at the tellurium atom does not influence appreciably the yields of the arylated olefins. The reaction proceeds analogously also when rhenium(III) and rhodium(III) chlorides are used, but the yields of the olefins (XX) are then somewhat lower. Like diaryltellurium dihalides, aryltellurium trichlorides (XXV) give rise to *trans*-stilbenes on interaction with styrene:[32]



(XXV) (XX) (XXI)

Ar=Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$.

The olefin arylation reactions can be carried out also in catalytic amounts of $PdCl_2$, provided that a suitable oxidant is added to the reaction mixture: t-butyl hydroperoxide or copper(II) chloride (which is especially effective in solution in acetic acid). As in the case of mercury derivatives,[36,37] the arylation of olefins by organotellurium compounds proceeds via reactive arylpalladium intermediates (XXVI), which can either add to the double bond with subsequent β-elimination of HPdX (or BrPdX in the case of allyl bromides) or undergo reactive dimerisation with formation of biaryls (XXI). Both these reactions pathways can be illustrated in relation to the arylation of methacrylonitrile by diphenyltellurium dichloride in the presence of palladium(II) salts:[32]



Analogously to σ-telluranes, the interaction of diphenyl telluride with ethyl acrylate in the presence of $Pd(OCOCH_3)_2$ leads to ethyl cinnamate together with a certain amount of biphenyl.[22]

(*e*) *Geometrical Isomerisation of Olefins*

An interesting application of organyltellurium trichlorides is their use for the geometrical isomerisation (inversion) of olefins by coupling *cis*-tellurotrichlorination and *trans*-dechlorotelluration processes.[33] When olefins interact with one equivalent of $TeCl_4$ in acetonitrile or chloroform,[33,43–45] 2-chloroalkyltellurium trichlorides (XXVII) are formed in high yields. The reduction of these compounds with an aqueous solution of Na_2S leads to the liberation of elemental tellurium and the reformation of the initial olefin, but this time in the form of a mixture of *E*- and *Z*-isomers with the inverted form predominating. Thus the reaction involving *E*-but-2-ene yielded but-2-ene with the isomer ratio *Z* : *E* = 97 : 3.[33] The ratio of the isomers formed depends on the nature of the olefin and the solvent employed.

(III) (XXVII a-c) (III)

a) $R = n\text{-}C_8H_{17}$, $R' = H$; b) $R = n\text{-}C_8H_{17}$, $R' = D$; c) $R = R' = Me$.

The preferential *cis*-addition to the olefin has been demonstrated by studying the ^1H NMR spectra of the products of the addition of the $TeCl_4$ to *E*-[1-D]dec-1-ene.[33]† When this mixture is reduced with an aqueous solution of Na_2S, a mixture of the *Z*- and *E*-[1-D]dec-1-enes (85 : 15) is formed in

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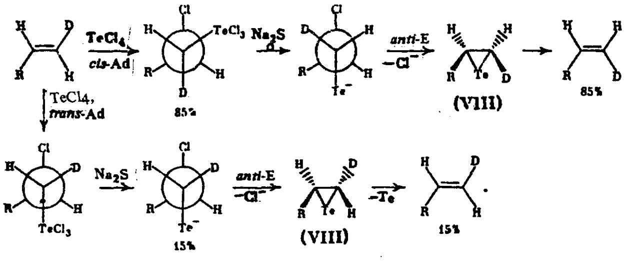
† The formation of 15% of the *trans*-adduct can be explained according to the authors[33] by the contribution of the electrophilic addition of $TeCl_4$, having the structure $TeCl_3^+Cl^-$ according to Krebs et al.[47]

conformity with stereospecific anti-elimination, which probably proceeds via the epitelluride (VIII):

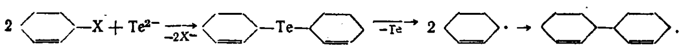


(f) Synthesis of 1,5-Dienes

When diphenyl telluride is heated with allyl bromide at 180 °C in a sealed tube, diphenyltellurium bromide and diallyl are formed:[21]

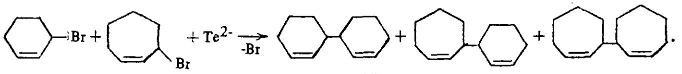
$$Ph_2Te + H_2C{=}CHCH_2Br \rightarrow Ph_2TeBr_2 + H_2C{=}CHCH_2CH_2CH{=}CH_2 .$$

However, a more promising method of synthesis of 1,5-dienes of type (XXVIII) involves the interaction of alkyl halides of the allyl type with lithium telluride in boiling THF or a dioxant–THF mixture.[48] According to the data of Clive et al.,[48] the reaction proceeds via the initial formation of dialkenyl tellurides of type (XXIX) with their subsequent decomposition into radicals of the allyl type, which then dimerise:



(XXIX) (XXVIII)

This mechanism has been confirmed by the finding that the interaction of a mixture of 3-bromocyclohexene and 3-bromocycloheptene with the Te^{2-} anion yields an almost statistical mixture of 2,2'-bicyclohexenyl (XXVIII), 3-(2'-cyclohexenyl)-cycloheptene (XXX), and 2,2'-bicycloheptenyl (XXXI) in proportions of 1 : 1.2 : 1:[33]



(XXVIII) (XXX) (XXXI)

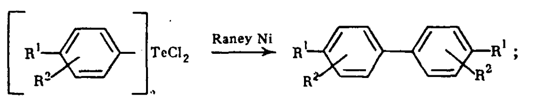
In contrast to dicycloalkenyl tellurides (XXIX), their selenium analogues are extremely stable. Thus the interaction of 3-bromocyclohexene with the Se^{2-} anion under conditions analogous to those examined above leads mainly to the selenium analogue of compound (XXIX); in addition, a small amount of 2,2'-bicyclohexenyl (2%) is formed.[33]

3. Biaryls

One of the first examples of the application of organotellurium compounds in organic synthesis is in the synthesis of biaryls by the reductive cleavage of derivatives of tetracoordinate[32,49,50] and dicoordinate tellurium.[22,49–51] Although biaryls are formed (together with diaryl tellurides) also on thermal decomposition of tetra–aryltellurium derivatives Ar_4Te (Ar = Ph,[52,53] C_6F_5,[54] or 4-MeC_6H_4 [53]), the latter reaction cannot be regarded as of preparative significance because the starting compounds for the synthesis of the tetra-aryltellurium derivatives are diaryltellurium dichlorides, from which biaryls can be obtained directly (see below).

(a) Reactions of Derivatives of Tetracoordinate Tellurium with Raney Nickel

When diaryltellurium dichlorides (IX, X = Cl) are treated with degassed Raney nickel in methylcellosolve, the biaryls (XXI) are obtained in good yields (58–91%).[49] The use instead of degassed Raney nickel of a catalyst obtained by boiling commercial nickel in 2-methoxyethyl ether or ethylene glycol gives rise to lower and less reproducible yields of biaryls:[49]



(IX) (XXI)

R^2 = H, R^1 = OMe, OEt, H, Me, Br, 4-Me_2N; R^1 = OMe,
R^2 = 3-Me, 3-OMe, 2-OMe; R^1, R^2 = 3,4-C_4H_4 .

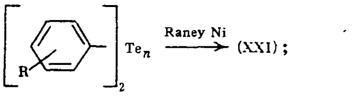
Aryltellurium trichlorides (XXV) are less suitable for the synthesis of biaryls,[49] although in the case of 2-naphthyltellurium trichloride, the yield of 2,2'-binaphthyl is 98%.[50]

(b) Reactions of Derivatives of Tetracoordinate Tellurium with Palladium(II) Salts

It was already mentioned above that, when olefins are arylated by diphenyl telluride[22] and σ-telluranes[32] in the presence of palladium(II) salts, the biaryls (XXI) are formed as side products together with arylated olefins. If the reactions of σ-telluranes (1 mol) with palladium(II) salts (2 mols) are carried out in the absence of olefins, then the arylpalladium intermediates (XXVI) undergo reductive dimerisation and the biaryls (XXI) are formed as sole products in moderate yields.[32]

(c) Reactions of Derivatives of Dicoordinate Tellurium with Raney Nickel

Like σ-telluranes,[49,50] the diaryl tellurides (I, $R^1 = R^2 =$ Ar) and diaryl ditellurides (V) are converted into the biaryls (XXI) in high yields (60–90%) on treatment with degassed Raney nickel:



(I), n = 1; (V), n = 2
R = 4-OMe, H, 4-Me, 4-OEt, 4-Br.

(d) Reactions of Diaryl Tellurides with Organomagnesium Compounds

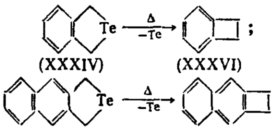
Another way of using diaryltellurides (I) in the synthesis of the biaryls (XXI) involves their treatment of Grignard reagents in ether or THF in the presence of phosphine complexes of nickel and cobalt [$NiCl_2(PPh_3)_2$, $NiCl_2(Ph_2PCH_2CH_2.$ $.PPh_2)$, and $CoCl_2(PPh_3)_2$], which leads to the cross-coupling products (XXXII) and the homo-coupling products (XXXIII) together with the biaryls:[51]

$$\underset{(I)}{Ar_2Te} + RMgBr \xrightarrow{Ni(II)\ or\ Co(II)} \underset{(XXXII)}{Ar{-}R} + \underset{(XXI)}{Ar{-}Ar} + \underset{(XXXIII)}{R{-}R} .$$

The reaction mechanism proposed by Uemura and Fukuzawa[51] includes the formation of diorganylnickel (or diorganylcobalt) complexes, their subsequent conversion, on treatment with diaryl tellurides, into aryltelluronickel (or the corresponding cobalt) complexes, and the decomposition of the latter with the elimination of tellurium and the formation of the final products.

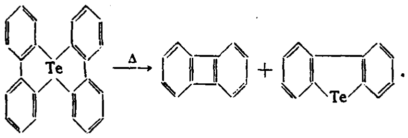
4. Cyclic Hydrocarbons

The synthesis of cyclic hydrocarbons of various types with the aid of organotellurium compounds is based on the ease of elimination of elemental tellurium from the corresponding tellurium-containing heterocycles.[55,56] For example, the thermal decomposition of compounds (XXXIV) and (XXXV) leads to benzo[*b*]cyclobutene (XXVI) and naphtho[*b*] cyclobutene in high yields:[55]



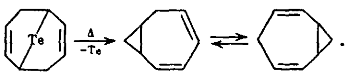
(XXXIV) (XXXVI)
(XXXV) (XXXVII)

Like cyclic tetra-aryltellurium derivatives,[52–54] bis(diphenylene)tellurium(XXXVIII) gives rise on thermolysis to a heterocyclic diaryl telluride—dibenzotellurophen (yield 96%) and biphenylene (XXXIX) (yield 52%).[57,58] Together with the latter compound, also traces of polyphenylenes were detected in this reaction:



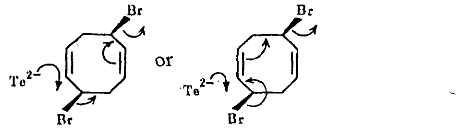
(XXXVIII) (XXXIX)

In certain cases processes of the type considered are accompanied by rearrangements. Thus, when 9-tellurabicyclo[3.3.1]nona-2,6-diene (XL) is heated in deuteriotoluene (in a sealed tube) at 175 °C, bicyclo[5.1.0]octa-2,5-diene (XLI) is formed in a quantitative yield[56] and is in equilibrium with its isomeric diene (XLIa):



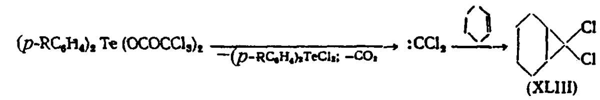
(XL) (XLI) (XLIa)

It is noteworthy that compound (XLI) is capable of being formed (in 20% yield) [together with compound (XL) in 18% yield] also under conditions ruling out the possibility of the thermal decomposition of compound (XL), on interaction of the dibromide (XLII) with Na_2Te in dimethylformamide (DMF), which the authors[56] explain by the following scheme



(XLII) (XLII)

Diaryltellurium bis(trichloroacetate) (IX, X = $OCOCCl_3$) decomposes on heating with formation of diaryltellurium dichlorides (IX, X = Cl), carbon dioxide, and dichlorocarbene,[59] which makes it possible to employ them for the synthesis of dichlorocyclopropanes. When compound (IX) is refluxed in the presence of cyclohexene in *p*-xylene (or diglyme, 2,2-dichlorobicyclo[4.1.0]heptane (XLIII) is formed in low yields (20–30% together with diaryltellurium dichlorides (60–70%):[59]



(XLIII)

R=H, Me, OMe, Me_2N.

III. SYNTHESIS OF HALOGENO-DERIVATIVES

The formation of mono- and di-halogeno derivatives of various types is frequently observed in reactions involving σ-telluranes.[43,44,60–65] However, these processes are by no means equivalent as regards preparative importance and some of them, for example, the formation of alkyl halides on thermal decomposition of alkylphenyltellurium dihalides[60] and di(chloroalkyl)- and di(chlorocycloalkyl)-tellurium dichlorides,[43,44,61] are relatively unpromising. Indeed alkyl phenyl tellurides, which are the starting materials in the synthesis of alkylphenyltellurium dihalides, are obtained by the reaction of tellurophenoxide anions with alkyl halides, while the pyrolysis of di(chloroalkyl)- and di(chlorocycloalkyl)-tellurium dichlorides results in the formation of a series of side products together with halogeno-derivatives of different structure.

1. Aromatic Halogeno-derivatives

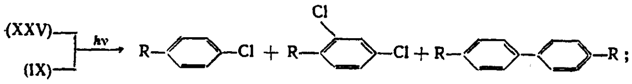
Aromatic halogeno-derivatives are formed on photolytic[62] or hydroperoxide-induced α-elimination[63] and also on elimination of tellurium halides (by treatment with bromine or iodine) from σ-telluranes of the type Ar_2TeX_2 and $ArTeX_3$.[64]

(a) *Photolytic α-Elimination from σ-Telluranes*

Reactions involving photolytic α-elimination of organyl halides from σ-telluranes are fairly general and lead to the formation of aromatic monohalogeno-derivatives and also dihalogeno-derivatives of cyclic and ethylenic hydrocarbons[62] (see below).

p-Chloroanisole (XLIV, R = OMe, X = Cl) is formed in a high yield (70%) together with small amounts of 2,4-dichloroanisole (XLV, R = OMe, X = Cl) and 4-methoxybiphenyl (XXI) (1%) on photolysis of *p*-anisyltellurium trichloride (XXV, R = OMe, X = Cl) in benzene. Metallic tellurium is liberated during the reaction probably as a consequence of the disproportionation of the $TeCl_2$ formed initially.[62] Other aryltellurium dichlorides behave analogously. In the reactions of diaryltellurium dichlorides, the yield of aryl halides is reduced; instead of elemental tellurium, a mixture of inoganic and organic tellurium compounds of unknown structure is produced and the amount of asymmetric biaryls increases.

p-Anisyltellurium tribromide, di(*p*-anisyl)tellurium diacetate, and *p*-anisyltellurium triacetate [obtained *in situ* from di(*p*-anisyl) ditelluride and lead tetra-acetate] enter into analogous reactions, which lead to *p*-anisyl bromide and p-anisyl acetate in yields of 30% and 6 and 15% respectively:[62]



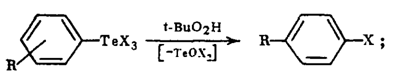
(XLIV) (XLV) (XXI)

X=Cl, R=OMe, Me.

The selective formation of the C–X bond (X = Hal) in the *unco*-positions [2- and 4-positions (Ed.of Translation)] in the molecule and the limited involvement of the solvent (benzene) in the formation of products (low yield of biaryls) suggest that the photolysis of σ-telluranes considered here does not entail the formation of free radicals. This is also indicated by the finding that the ratio of the reaction products does not change significantly in the photolysis of *p*-anisyltellurium trichloride or di(*p*-anisyl)tellurium dichloride in the presence of t-butyl peroxide.[62]

(b) α-Elimination Induced by Hydroperoxides

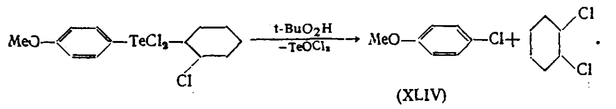
After the acetic acid solution of *p*-anisyltellurium trichloride (XXV, R = *p*-Ome, X = Cl) (1 mol) and t-butyl hydroperoxide (2 mols) has been refluxed for a short time, *p*-chloroanisole (XLIV) is obtained in 53% yield.[63] Tellurium is then converted into tellurium oxide chlorides, although the structure of the inorganic products has not been accurately established:[63]



(XXV) (XLIV)

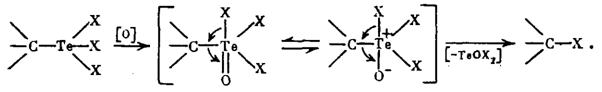
X = Cl, R = OMe, 4-Me, 2.3-C_4H_4; X = Br, R = 4-OMe .

When 2-chlorocyclohexyl-*p*-methoxyphenyltellurium dichloride is treated with t-butyl hydroperoxide in acetic acid, a mixture of *p*-chloroanisole (22%) and 1,2-dichlorocyclohexane (55%) (configuration not indicated) is formed, which indicates a greater liability of the C_{Alk}–Te bonds in the α-elimination reactions compared with C_{Ar}–Te:



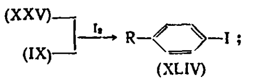
(XLIV)

The authors[63] suggest that organyl halides are formed via a mechanism involving the 1,2-tellurium halide shift in an instable hexacoordinate tellurium derivative formed on oxidation of σ-telluranes:



(c) Reactions Involving the Halogen-induced Elimination of Tellurium from σ-Telluranes

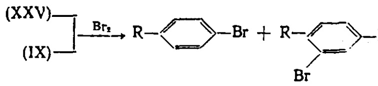
When *p*-anisyltellurium trichloride (XXV) reacts with iodine in boiling acetonitrile, *p*-iodoanisole (XLIV, X = I) is formed in 13% yield;[64] the presence of the *o*- and *m*-isomers was not detected under these conditions. The introduction of potassium, caesium, or ammonium fluorides into the reaction mixture increases the yield of *p*-iodoanisole to 85%. Treatment of diaryl tellurium dichlorides (IX, X = Cl) under analogous conditions also leads to aryl iodide, but in lower yields. On passing from *p*-anisyl- to phenyl- and *p*-bromphenyl-tellurium trichlorides, the yields of aryl iodides fall sharply, which indicates the electrophilic character of the process. The nature of the electronegative substituents at the tellurium atom (Cl, OCOMe, and $OCOCF_3$) does not have a significant influence on the yields of aryl iodides:[64]



(XLIV)

X=Cl, R=OMe, Me, H; X=OAc, R=OMc, H; X=$OCOCF_3$, R=H.

Somewhat different results have been obtained in the study of the elimination of tellurium bromide from σ-telluranes.[64] In the reaction of *p*-anisyl-tellurium trichloride with bromine in different solvents (actonitrile, dioxan, acetic acid), mainly 2,4-dibromoanisole (XLV, R = OMe, X = Br) and a small amount of *p*-bromoanisole (XLIV, R = Ome, X = Br) are formed. The preferential formation of the dibromo-derivatives (XLV) from *p*-anisyltellurium trichloride is the result of the ready bromination of the monoaryl bromides (XLIV) formed initially in the presence of tellurium(IV) derivatives playing the role of catalysts of electrophilic substitution in the aromatic ring. As in the elimination of tellurium iodide, the weakening of the electron-donating properties of the substituent in the arene rings (phenyl- and *p*-bromophenyl-tellurium trichlorides) leads to a sharp decrease of the yield of aryl bromide even in the presence of caesium and ammonium fluorides:[64]



(XLIV) (XLV)

R=OMe, Me, H .

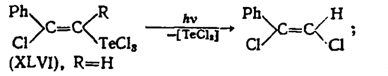
The chlorine-induced elimination of tellurium from aryltellurium trichlorides by reaction with chlorine, $SbCl_5$, and t-butyl hypochlorite affors very low yields of aryl chloride even in the case of *p*-anisyltellurium trichloride (not more than 5%). The cyanide-induced elimination of tellurium from aryltellurium trichlorides by reaction with copper(I) cyanide in DMF proceeds in approximately the same manner (yield 8%).[63]

2. Dihalogeno-derivatives of Olefinic and Cyclic Hydrocarbons

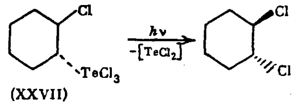
The formation of derivatives of organic compounds of these classes has been observed in the same reactions as the formation of aryl halides: photolytic[62] and hydroperoxide-induced α-elimination from σ-telluranes[63] and also halogen-induced elimination of tellurium from 2-chlorovinyltellurium trichlorides.[65]

(a) Photolytic α-Elimination

Irradiation of a benzene solution of *Z*-2-chlorovinyl-2-phenyltellurium trichloride (XLVI, R = H) with UV light leads to *Z*-1,2-dichloroethylene (yield 39%); the composition and structure of other reaction products were not established; this may indicate that the α-elimination proceeds in this case with retention of configuration.[62] The photolysis of *trans*-2-chlorocyclohexyltellurium trichloride (XXVII) results in the formation of *trans*-1,2-dichlorocyclohexane in 28% yield[62] (the formation of the *cis*-isomer was not observed):



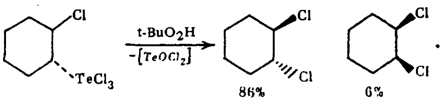
(XLVI), R=H



(XXVII)

(b) α-Elimination Induced by Hydroperoxides

Dihalogeno-derivatives of the types considered can be formed also by the hydroperoxide-induced α-elimination of organic halides from organyltellurium trihalides.[63] Thus, when *trans*-2-chlorocyclohexyltellurium trichloride is briefly refluxed with two equivalents of t-butyl hydroperoxide, a mixture of *trans*- and *cis*-1,2-dichlorohexanes is formed in yields of 86% and 6% respectively:

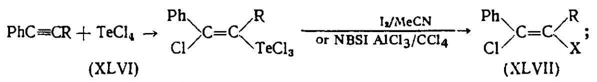


The analogous reaction with *trans*-2-chlorocyclohexyltellurium triiodide, which leads to only *trans*-1,2-chlorodiiodocyclohexane (64%), takes place also when t-butyl hydroperoxide is replaced by hydrogen peroxide, cumenyl hydroperoxide, and *m*-chloroperbenzoic acid, but the yields are then appreciably lower.[63]

Z-1,2-dichloroethylenes are formed together with small amounts of the *E*-isomers (ratio approximately 9 : 1) in the reaction involving *Z*-2-chlorovinyltellurium trichlorides (XLVI, R = H or Ph).[63]

(c) Halogen-induced Elimination of Tellurium from 2-Chlorovinyltellurium Trichlorides

The halogen-induced elimination of tellurium from 2-chlorovinyltellurium trichlorides (XLVI), whose *Z*-isomers are readily obtained (in 80–90% yield) by the addition of $TeCl_4$ to substituted acetylenes, has been used to synthesise 1,2-dihalogenoethylenes. Thus the iodine-induced elimination of tellurium from compounds (XLVI) by treatment with iodine (in acetonitrile or methanol) and the bromine-induced elimination of tellurium by treatment with *N*-bromosuccinimide (NBSI) ($NBSI/AlCl_3$ in CCl_4 or $NBSI/CuBr_2$ in acetonitrile) proceeds with retention of configuration, as for many β-substituted vinyl organometallic compounds investigated previously, and leads to *Z*-1,2-chloroiodo(or bromo)ethylenes (XLVII) in high yields:[65]



$$PhC{\equiv}CR + TeCl_4 \rightarrow \underset{\text{(XLVI)}}{\overset{Ph}{\underset{Cl}{}}\!\!>C{=}C<\!\!\overset{R}{\underset{TeCl_3}{}}} \xrightarrow[\text{or NBSI AlCl}_3/\text{CCl}_4]{I_2/MeCN} \underset{\text{(XLVII)}}{\overset{Ph}{\underset{Cl}{}}\!\!>C{=}C<\!\!\overset{R}{\underset{X}{}}};$$

X=I, R=H, Me, Et, Ph; X=Br, R=H, Ph.

Bearing in mind that, in contrast to other reagents (for example $HgCl_2$ [66]), which give rise to *E*-isomers as a result of *trans*-attack, the addition of $TeCl_4$ to substituted acetylenes always leads to *Z*-isomers (XLVI) and that the elimination of tellurium from the latter proceeds with retention of configuration, the above reaction sequence can be regarded as a convenient method of synthesis of *Z*-chloro(or bromo)-alkanes from alkynes.

(d) Dihalogeno-derivatives of Saturated Hydrocarbons

A single example of the synthesis of dihalogeno-derivatives of this type in reactions of organotellurium compounds has been described, namely the formation of 1,1-dibromoalkanes in high yield or thermal decomposition of 1,1-bis(phenyldibromotelluro)alkanes in the presence of sodium bromide in DMF.[63] The initial compounds are obtained in 80–85% yield by the reaction of alkyl halides with bis(phenyltelluro)methyllithium[67] and subsequent bromination of the intermediate bistellurides:

$$RX \xrightarrow[2)\ Br_2]{1)\ LiCH(TePh)_2} RCH\,(TeBr_2Ph)_2 \xrightarrow{NaBr} RCHBr_2\,;$$
$$R{=}C_{11}H_{23},\ C_{12}H_{25},\ C_{14}H_{29},\ C_{16}H_{33},\ Ph\,(CH_2)_3\,.$$

IV. SYNTHESIS OF CARBONYL COMPOUNDS

Carbonyl compounds of different classes, namely aldehydes,[60,68,69] ketones,[15,16,70–72] and carboxylic acids[72,73] and their derivatives (esters[15,16,70,74–76] and anhydrides[59,77,78]) can be formed in reactions of monocoordinate,[71,72] dicoordinate,[69] tricoordinate,[15,16,70,76,78] and tetracoordinate[59,68,73–75,77] derivatives of tellurium.

1. Aldehydes

Benzaldehyde (together with other compounds) is formed in the photochemical oxidation of dibenzyl telluride or dibenzyl ditelluride.[69] Bis(*p*-methoxyphenyl)tellurone ($(p\text{-}RC_6H_4)_2.$ $.TeO_n$ (XLVIII, R = OMe, *n* = 2)—the first reliably characterised representative of tellurone obtained by the oxidation of bis(*p*-methoxyphenyl) telluroxide (XLVIII, *n* = 1) with sodium periodate, is an effective oxidant oxidising various substituted benzyl alcohols to the corresponding benzaldehydes.[68] Thus the oxidation of piperonyl and veratryl alcohols by compound (XLVIII, *n* = 2) gave 70–80% yields of piperonyl and veratryl aldehydes.[68] Aldehydes have also been obtained in 70–93% yield by treating bis(phenyldiiodotelluro)alkanes (XLIX) [60] with NaI in DMF under mild conditions (60 min, 20 °C):

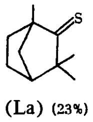
$$\underset{\text{(XLIX)}}{RCH\,(TeI_2Ph)_2} \xrightarrow{NaI} RCHO\,;$$
$$R{=}C_{11}H_{23},\ C_{12}H_{25},\ C_{14}H_{29},\ C_{16}H_{33},\ Ph\,(CH_2)_3\,.$$

2. Ketones

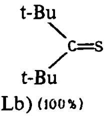
Ketones are formed when thioketones (L) are oxidised[15,16,70] by diaryl telluroxides (XLVIII, *n* = 1) and on reduction of α-halogenoketones with *OO*-diethyl phosphorotellurolates (VII) [71] or alkali metal tellurophenoxides (IV).[72]

(a) Oxidation of Thiocarbonyl Compounds by Diaryl Telluroxides

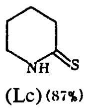
Thioketones with a wide variety of structures (L a–d) can be selectively oxidised to ketones with the aid of diaryl telluroxides[15,16,70] (under the formula of each thiocarbonyl compound given below, the yield of its oxo-analogue is indicated). Together with oxo-compounds, sulphur and diaryl tellurides are formed in these reactions in almost quantitative yields:



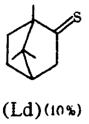
(La) (23%)



(Lb) (100%)

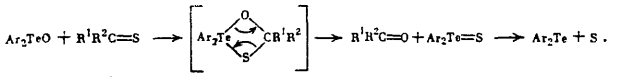


(Lc) (87%)

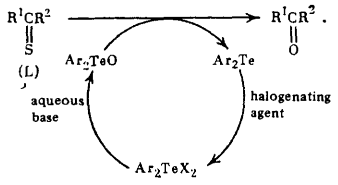


(Ld) (10%)

According to Ley et al.,[16] the mechanism of this reaction can be represented schematically as follows:



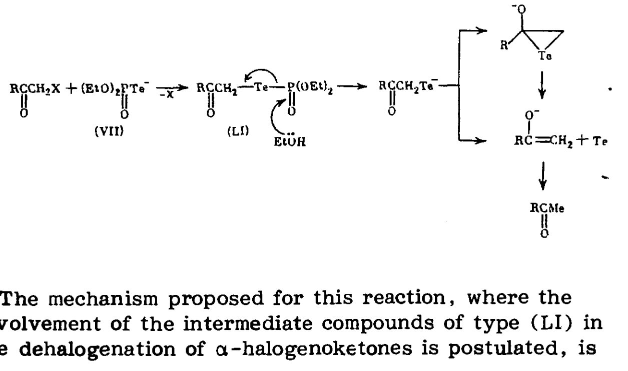
The oxidation of thioketones and thioacid esters (see below) to the corresponding oxo-derivatives has also been achieved with the aid of the catalytic oxidation-reduction cycle,[16,70] which requires the presence of a mild and effective halogenating agent into convert diaryl tellurides (I) into diaryltellurium dihalides (IX) and an aqueous solution of a base capable of converting the latter into diaryl telluroxides (XLVIII, $n = 1$). The most suitable brominating agent for tellurides is 1,2-dibromotetrachloroethane, which converts them into tellurium dibromides (IX, X = Br) in high yields at room temperature. Other reagents, namely hexachloroacetone, tetrabromoethane, and the dibromide of Meldrum's acid were much less effective in the above catalytic cycle. Among bases, an aqueous solution of potassium carbonate proved the most effective.[16,70] The optimum conditions in this reaction are stirring at room temperature in chloroform of a mixture of the carbonyl compound, 1.5% of the telluride (tellurium dihalides) or telluroxide, an excess of 1,2-dibromotetrachloroethane, and an aqueous solution of K_2CO_3:



The study of the influence of the nature of organic groups in the molecules of diaryltellurium dichloride $R^1C_6H_4TeCl_2.C_6H_4R^2$ used in this catalytic cycle showed that, as the electron-donating properties of the ring substituents R^1 and R^2 in the *p*-positions with respect to the tellurium atom are enhanced, the rate of the oxidation reaction increases in the following sequence: H,H < 4-MeO,4′-MeO < 4-MeO,4′-NMe_2 < 4NMe_2,4′-NMe_2.

(b) *Reduction of Ketones with Functional-group Substituents in the α-Position*

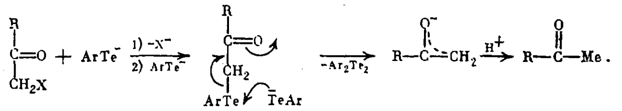
Sodium *OO*-diethyl phosphorotellurolate (VII) is a mild dehalogenating reagent for various α-halogenoketones.[71] Best results have been achieved in this reaction using stoichiometric amounts of the reactants in ethanol or THF (20° to 80 °C):



The mechanism proposed for this reaction, where the involvement of the intermediate compounds of type (LI) in the dehalogenation of α-halogenoketones is postulated, is based on the fact that the analogous reaction of 2,4′-dibromoacetophenone with sodium *OO*-diethyl phosphoroselenolate entails the formation of the selenium analogue of compound (LI), which does not, however, undergo further reactions.[71]

The readily available lithium and sodium thiophen-2-tellurolates, obtained by the reaction of 2-lithiothiophen with tellurium in THF or by the reduction of di(2-thienyl) ditelluride in an alkaline solution of $NaBH_4$ in alcohol, are extremely convenient, in the preparative sense, dehalogenating agents for various α-halogenoketones.[72]

The interaction of tellurophenoxides (2 mols) with α-halogenoketones (1 mol) results in reduction and the formation in high yields of the corresponding ketones and di(α-thienyl) ditelluride. In contrast to the reactions of α-halogenoketones with thiolate and selenolate anions, which usually give rise to a mixture of reduction and substitution products,[79,80] the use of the thiophen-2-tellurolate anion results in the formation of only the reduction products. However, it is possible that nucleophilic substitution with formation of intermediates of type (LII) is an intermediate stage in the reduction of α-halogenoketones by tellurolate anions. An indirect confirmation of this is provided by the interaction of α-bromoacetanilide (in excess) with sodium thiophen-2-tellurolate in alcohol, which results in the isolation of α-(2-thienyltelluro)acetanilide in 64% yield. This confirms the possibility, in principle, of the formation of the intermediate substitution product (LII) also in the reaction of $ArTe^-$ with α-halogenoketones and suggests the following two-stage reduction mechanism:[72]



A number of other electronegative substituents, for example, the MeCOO, $MeSO_2O$, and PhS groups, can also be readily removed from the α-position in acetophenones on treatment with alkali metal thiophen-2-tellurolates.[71]

In many cases α-halogenoketones may be reduced by employing sodium tetrahydroborate as the reducing agent in the presence of catalytic amounts of di(2-thienyl) ditelluride,[72] similarly to the formation of olefins by the reduction of vicinal dibromides examined above.[18]

3. Quinones

The formation of quinones with the aid of organotellurium compounds is based on the oxidation of dihydric phenols by diaryl telluroxides (XLVIII, $n = 1$)[15,16] or diaryl tellurones (XLVIII, $n = 2$).[68] Thus the oxidation of hydroquinone,[16] 1,4-dihydronaphthalene,[16] and 3,5-di-t-butyl-1,2-dihydroxybenzene[15,16] by di(*p*-anisyl) telluroxide leads to *p*-benzoquinone, 1,4-naphthoquinone, and 3,5-di-t-butyl-*o*-benzoquinone in 65, 97, and 80% yields respectively. In the case of di(*p*-anisyl)tellurone, the yield of *p*-benzoquinone is smaller, amounting to only 39%.[68]

4. Carboxylic Acids

(a) *Carbonylation of σ-Telluranes*

One of the possible ways of obtaining carboxylic acids from organotellurium compounds is based on the interaction of diaryltellurium dichlorides or aryltellurium trichlorides with nickel carbonyl in DMF at 70 °C and subsequent treatment with water:[73]

$$Ar_2TeCl_2 + Ni(CO)_4 + 2H_2O \rightarrow 2ArCOOH + NiTe + 2HCl + 2CO;$$
$$ArTeCl_3 + 2Ni(CO)_4 + H_2O \rightarrow ArCOOH + NiCl_2 + NiTe + HCl + 7CO.$$

Together with carboxylic acids, diarylketones and diaryl tellurides are formed in this instance as side products.

By analogy with familiar reactions of this type involving other metallic compounds, their possible mechanisms can be described by the following schemes:[73]

(1) Aryltellurium trichlorides:

$$ArTeCl_3 + Ni(CO)_4 \rightarrow NiCl_2 + ArTeNi(CO)_2Cl \xrightarrow[ArTeCl_3]{\text{arylation}} Ar_2Te, \qquad (1)$$

$$ArTeNi(CO)_2Cl + Ni(CO)_4 \rightarrow NiTe + ArNi(CO)_2Cl, \qquad (2)$$

$$ArNi(CO)_2Cl + Ni(CO)_4 \xrightarrow{\text{insertion}} \underset{\overset{\|}{O}}{ArC}Ni(CO)_2Cl - \left[\begin{array}{l} \xrightarrow{\text{arylation}} Ar_2CO, \\ \xrightarrow[H_2O]{} ArCOOH. \end{array}\right. \qquad (3)$$

(2) Diaryltellurium dichlorides

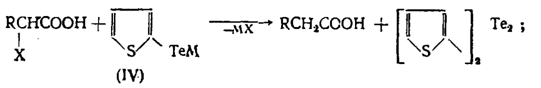
$$Ar_2TeCl_2 + Ni(CO)_4 \rightarrow ArNi(CO)_2Cl + ArTeNi(CO)_2Cl,$$

followed by reactions (1), (2), and (3).

Aliphatic tellurium dichlorides, in particular di(2-chloropropyl)tellurium dichloride, decompose under analogous conditions with formation of alkenes (in the given instance, propene), $NiCl_2$, and NiTe.[73] When $Ni(CO)_4$ is replaced by $Fe_2(CO)_9$, carbonylation does not take place. Thus the reaction of p-anisyltellurium trichloride with $Fe_2(CO)_9$ results in the formation of only di(p-anisyl) ditelluride, apparently as a consequence of the reduction of the trichloride by iron carbonyl.[73]

(b) Reduction of Carboxylic α-Halogenoacids

Like α-halogenoketones (see above), carboxylic α-halogenoacids are reduced in high yields by lithium and sodium thiophen-2-tellurolates (IV) to the corresponding carboxylic acids:[72]



(IV)

M=Li, Na; R=Ph (99%), 1-$C_{10}H_7$ (97%), $(Ph)_2$ (98%).

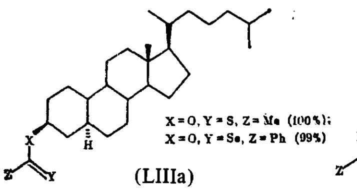
5. Derivatives of Carboxylic Acids

Organotellurium compounds have been used to obtain derivatives of carboxylic acids such as esters[15,16,70,74–76] and anhydrides.[77,78]

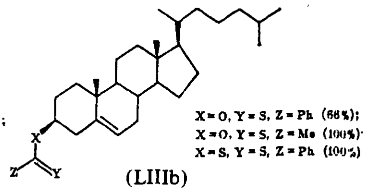
(a) Esters

Esters have been synthesised from derivatives of tricoordinate tellurium (diaryl telluroxides[15,16,70] and telluronium ylides[76]) and derivatives of tetracoordinate tellurium—diaryltellurium diacylates.[74,75]

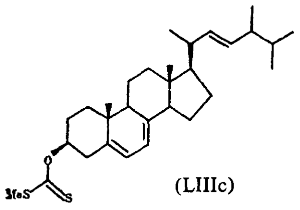
Diaryl telluroxides. Like ketones (see above), many esters were obtained in high yield by the oxidation of the corresponding thio- and selenocarbonyl compounds (LIIIa–e) with diaryl telluroxides:[15,16,70]



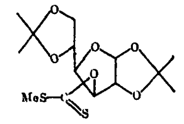
(LIIIa)



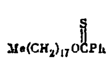
(LIIIb)



(LIIIc)



(LIIId)



$$Me(CH_2)_{17}O\overset{\overset{S}{\|}}{C}Ph$$

(LIIIe) 91%

Telluronium ylides. An effective method of synthesis of αβ-unsaturated acid esters is the interaction of carbonyl compounds with dialkyltelluronium ethoxycarbonylmethylylides (LV) obtained *in situ* by treating dibutylethoxycarbonylmethyltelluronium bromides (LVI) with potassium t-butoxide in THF. This reaction proceeds with high stereoselectivity, especially with aldehydes, and leads mainly to *E*-isomers:[76]

$$\underset{Br^-}{(C_4H_9)_2Te^+CH_2COOEt} \xrightarrow[THF]{Me_3COK} \underset{(LV)}{(C_4H_9)_2Te^+-\bar{C}HCOOEt} \xrightarrow[-(C_4H_9)_2TeO]{R^1R^2C=O}$$
$$\longrightarrow \underset{(LIV)}{R^1R^2C=CHCOOEt}.$$

The reaction is also applicable to cyclic and αβ-unsaturated ketones and aldehydes. The sharp difference between the reactivities of the telluronium ylides (LV) and the corresponding sulphonium ylides is noteworthy. Thus dimethylsulphonium ethoxycarbonylmethylide does not react with simple ketones and aldehydes, while its reaction with αβ-unsaturated carbonyl compounds yields cyclopropanes.[81]

Diaryltellurium diacylates. The methyl esters of carboxylic acids are formed in 85–90% yields on hearing diaryltellurium diacylates (IX) with methyl iodide in sealed tubes at 100 °C:[75]

$$\underset{(IX)}{(p\text{-}RC_6H_4)_2Te(OCOMe)_2} + MeI \rightarrow (p\text{-}RC_6H_4)_2TeI_2 + MeCOOMe;$$

R=H, Me, OMe.

When diphenyltellurium diacetate reacts with chlorotrimethylsilane, diphenyltellurium dichloride is formed in a high yield (it is probably accompanied by trimethylsilyl acetate):[74]

$$Ph_2Te(OCOMe)_2 + 2Me_3SiCl \rightarrow Ph_2TeCl_2 + 2MeCOOSiMe_3.$$

(b) Acid Anhydrides

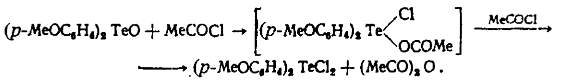
Carboxylic acid anhydrides have been obtained in 80–95% yields by the reaction of diaryltellurium diacylates (IX) with acyl chlorides:[59,77]

$$\underset{(IX)}{(p\text{-}R^1C_6H_4)_2Te(OCOR^2)_2} + 2R^2COCl \rightarrow (p\text{-}R^1C_6H_4)_2TeCl_2 + (R^2CO)_2O;$$

R^1=H, R^2=Me; R^1=Me, R^2=Ph; R^1=OMe, R^2=Et; R^1=OMe, R^2=CH_2Cl.

The high yields make it possible to regard this reaction as a preparative method of synthesis of the anhydrides of both aliphatic and aromatic carboxylic acids. The attempts to use it for the synthesis of mixed anhydrides were, however, unsuccessful. Thus, although treatment of di(p-anisyl)-tellurium bis(trifluoroacetate) with acetyl chloride afforded di(p-anisyl)tellurium dichloride in a yield exceeding 90%,[59,77] the asymmetric anhydride, namely acetyl trifluoroacetate, was not isolated, which can probably be accounted for by its disproportionation under the reaction conditions.

Anhydrides are also formed in the reaction of diaryl telluroxides with carboxylic acid chlorides, apparently via the intermediate formation of diaryltellurium chloroacylates:[78]



$$(p\text{-}MeOC_6H_4)_2TeO + MeCOCl \rightarrow \left[(p\text{-}MeOC_6H_4)_2Te\begin{matrix}Cl\\OCOMe\end{matrix}\right] \xrightarrow{MeCOCl} (p\text{-}MeOC_6H_4)_2TeCl_2 + (MeCO)_2O.$$

V. CONCLUSION

The data presented in the review demonstrate the likely usefulness of the application of organotellurium compounds in the synthesis of various classes of organic compounds and in the first place unsaturated and cyclic hydrocarbons, halogeno-derivatives of various types, and carbonyl compounds. Among these reactions, special interest attaches to catalytic reactions with participation of organotellurium compounds: tellurolate and phosphorotellurolate anions and diaryl telluroxides. In many instances the reactions which proceed readily when organotellurium reagents are used do not occur with selenium compounds having analogous structures (the synthesis of 1,5-dienes).

Further prospects for the application of organotellurium compounds in organic synthesis is as follows: (1) in the search for new possibilities of using organic derivatives of tellurium in order to obtain organic compounds, (2) in the study of conditions permitting an increase in the stereospecificity of the reactions, (3) in the development of new catalytic processes, and (4) in the elucidation of the specific features of organotellurium compounds compared with the analogous sulphur and selenium derivatives and in using these features in organic synthesis. The solution of the above problems is indissolubly linked to the expansion of studies connected with the development of methods of synthesis of organotellurium compounds using readily available starting materials and to the study of the reactivity of these compounds.

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During the preparation of this review for publication, a series of new reports on the application of organotellurium compounds in organic synthesis appeared. Uemura and Fukuzawa[82] gave a systematic account of and discussed the results of studies on the reaction involving α-elimination of organic halides from σ-telluranes of various types, published previously in a number of communications.[62,63,65] Olefins of different structure have been obtained in the decomposition of alkyl phenyl telluroxides synthesised either by the hydrolysis of the corresponding tellurium dibromides[83] or by the oxidation of alkylphenyl tellurides by hydrogen peroxide,[83] sodium periodate,[83] and m-chloroperbenzoic acid[83,84] and also by the catalytic debromination of vicinal dibromides by diaryl tellurides under the conditions of interfacial catalysis.[85] Catalytic debromination of 1,4-dibromoalk-2-enes by sodium thiophen-2-tellurolate has been used to obtain 1,3-dienes.[86] Oxidation of allyl phenyl tellurides by the oxidants enumerated above and also by t-butyl hydroperoxides leads to allyl alochols in high yields,[87] probably via the [2,3]-sigmatropic rearrangement of the alkyl phenyl telluroxides formed as intermediates.

New methods have been proposed for the synthesis of carboxylic acids on the basis of the decomposition of tellurones formed in the oxidation of ethylene ketals of aryl α-tellurophenylethyl ketones[88] and of the insertion (in the presence of $PdCl_2$) of the CO group in the Te–C bond in diorganyl tellurides and σ-telluranes.[89] New examples of the application of organotellurium reagents in the organic synthesis have been presented: the synthesis of αβ-unsaturated epoxides by the reaction of dialkyltelluronium allylides with aldehydes,[90] the synthesis of chlorohydrin ethers by the elimination of tellurium from the products of the addition of $TeCl_4$ to allyl ethers by treatment with Raney nickel,[91] and the formation of alkyl method ethers by the oxidation of alkyl phenyl tellurides with m-chloroperbenzoic acid in methanol.[92] Diaryl telluroxides proved to be effective catalysts of aldol condensation reactions[93] and diorganyl tellurides were found to catalyse the reactions of tosyl azide with aldehydes, which is due to the intermediate formation of tellurimides (from tosyl azide and diorganyl tellurides).[94]

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New Silylating Agents. Methods of Synthesis and Properties

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The methods of synthesis and properties of new silylating agents are examined and the results of studies on thier application in organic synthesis and in analytical chemistry are surveyed.
The bibliography includes 223 references.

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I. INTRODUCTION

Organosilicon compounds have found extensive applications in organic[1–13] and analytical[14–16] chemistry. One of the most important fields in which silicon-containing reagents are applied involves their use for silylation. The term "silylation" has come to be understood as the introduction of a triorganylsilyl, usually trimethylsilyl group, into the molecules of organic compounds instead of a mobile ("active") hydrogen atom or the metal atom replacing the latter.[14,17] The triorganylsilyl group is introduced into the organic molecule with the aid of the so called silylating agents, i.e. agents containing an Si–X bond, where X = O, N, S, C, or Hal, which is reactive with respect to a proton donor.

Silylation makes it possible to modify widely the physical and chemical properties of organic and organoelemental compounds: to protect or block certain reaction centres, to increase reactivity, to improve the solubility of substances in non-polar and weakly polar solvents, to reduce or to eliminate the possibility of the formation of hydrogen bonds, and to increase the volatility and stability of compounds.[14,18,19] Silylation is used for the purification of organic and organoelemental substances and also for their identification by physicochemical methods.[14,18,19]

Pierce's monograph[14] contains information about silylating agents and surveys data on the silylation of various classes of organic compounds published up to 1967. Later reviews,[17,18,20–25], devoted to a different aspect of silylation, also present the characteristics of silylating compounds.

In connection with the synthesis of a series of new effective silylating agents (silyl donors) and also the expansion of their applications, it became necessary to give a systematic account of and to survey data published mainly during the last 10 years. The present review is devoted to this topic.

II. SYNTHESIS AND PROPERTIES OF SILYLATING AGENTS

In recent years silylation has become an increasingly important method in synthetic organic chemistry, simplifying and improving the procedures for the preparation of many complex substances; many silylating agents, such as chlorosilanes and silazanes, are used in the large-scale industrial manufacture of antibiotics,[26,27] organosilicon monomers and polymers,[28] etc. Other silylating agents—silylated amines, amides, urea, sulphonic acids, and certain others—are widely employed in preparative synthesis.

Bearing in mind that silylation takes place with cleavage of the Si–X bond by the proton donor (HY), it is natural to arrange the silylating agents in groups in terms of the character of this bond.

1. Halogenosilanes (R_3Si–Hal)

In this group of silyl donors, chlorotrimethylsilane, which is widely used in industry, is most important.[28] The methods of its synthesis and also its silylating properties have been examined in books[14,28] and reviews.[17,20,21]

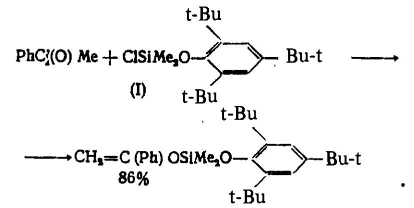
At the same time, the high sensitivity of the Me_3Si–O bond to hydrolysis, to attack by many nucleophiles, and also to hydrogenolysis[29] limits its employment in organic synthesis as a protecting group.[30,31] For this reason, silylating agents with bulkier groups at the silicon atom, for example t-butylchlorodiphenylsilane,[32] chlorotriisopropylsilane,[33,34] and especially t-butylchlorodimethylsilane, first used by Stork and Hudrlik,[35] have come to be employed more frequently in recent times. t-$BuMe_2SiCl$ is synthesised in accordance with the following scheme:[36,37]

$$Me_2SiCl_2 + t\text{-}BuLi \rightarrow t\text{-}BuMe_2SiCl + LiCl .$$

The t-$BuMe_2Si$–O bond is more resistant to hydrolysis than the Me_3Si–O bond (by a factor of 10^4) [38–40] and "withstands" reactions such as hydrogenolysis,[36] mesitylation,[41] phosphorylation,[42] reduction by diisobutylaluminium hydride,[46] oxidation by chromic acid in pyridine[43,44] or by ruthenium tetroxide,[44] and treatment by potassium t-butoxide in dimethylformamide (DMF),[45] Grignard[44] and Wittig[36] reagents, organocopper reagents,[46] and lithium in liquid ammonia.[44] The above group can be readily introduced into the organic molecule in the presence of imidazole,[47,48] *N*-dimethylaminopyridine,[49] or 1,8-diazabicyclo[5.4.0]undec-7-ene [50] as catalysts, after which it can be readily removed with the aid of sources of fluoride ions,[28] for example $Et_3N.HF$,[47] Bu_4NF,[51] KF/18-crown-6 ether,[31] and CsF/diglyme.[47] Bu_4NHSO_4/NaOH is sometimes used instead of tetrabutylammonium fluoride:[52]

$$ROH \xrightarrow[\text{imidazole/DMF}]{t\text{-}Bu_2Me_2SiCl} ROSiMe_2Bu\text{-}t \xrightarrow[\text{THF}]{Bu_4NF} ROH .$$

The 2,4,6-tri(t-butyl)phenoxydimethylsiloxy-group is even more resistant to the action of acids and bases. It is introduced into the organic molecule by treatment with the corresponding chlorosilane in the presence of sodium iodide and triethylamine in acetonitrile and is removed with the aid of potassium fluoride on celite:[53]



The chlorosilane (I) is a stable crystalline substance. It is obtained in 93% yield by the reaction of dichlorodimethylsilane with 2,4,6-tri(t-butyl)phenol and triethylamine on refluxing in acetonitrile.[53]

Silylation takes place extremely effectively in the presence of lithium sulphide in a polar medium:[54]

$$\mathrm{ROH + ClSiMe_2R' \xrightarrow[25^\circ]{Li_2S/MeCN} \underset{70-95\%}{ROSiMe_2R'}} \ ;$$

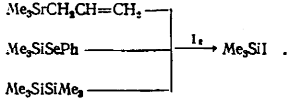
$\mathrm{R' = Me,\ t\text{-}Bu.}$

Bromotrimethyl- and especially iodotrimethyl-silanes are very active silylating agents;[55–58] they are obtained by cleaving the Si–O, Si–C, and other bonds with halogen, hydrogen halides, or the corresponding salts:[59–63]

$$\mathrm{Me_3SiOPh + Br_2 \xrightarrow{cat.} Me_3SiBr} \ ;$$

$$\mathrm{cat. = Zn, Al, Cu, Mg, Sn, Fe} \ ;$$

$$\mathrm{(Me_3Si)_2O \xrightarrow{AlI_3\ or\ Al/I_2} Me_3SiI + AlOI} \ ;$$



$$\mathrm{Me_3SrCH_2CH{=}CH_2,\ Me_3SiSePh,\ Me_3SiSiMe_3 \xrightarrow{I_2} Me_3SiI} \ .$$

However, Me₃SiBr and Me₃SiI are not often used for silylation because many functional groups are decomposed by them, for example, iodotrimethylsilane cleaves oxirans,[64,65] hydroxycyclanes,[66–68] ethers,[69,70] esters,[71–73] acetals, ketals,[73] etc.[74–78]

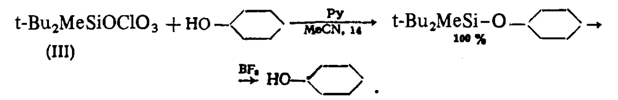
2. Reagents Containing the R_3SiO Group

Among silylating agents containing the Si–O bond, the most readily available compound is hexamethyldisiloxane. It is obtained by the hydrolysis of chlorotrimethylsilane.[28] As early as 1960,[79] it was shown that, in the presence of alkaline or acid catalysts, hexamethyldisiloxane is cleaved by alcohols and phenols, but, until recently it was believed that $(Me_3Si)_2O$ has no significant value as a silylating agent. The results of the study by Pinnick et al.[80] disproved this established view. It was found that the use of the pyridinium salt of toluenesulphonic acid Py.TosOH (II) greatly increases the effectiveness of hexamethylsiloxane as the silyl donor and makes it possible to obtain silyl ethers in yields up to 90%:

$$\mathrm{(Me_3Si)_2O + ROH \xrightarrow[\Delta,\ C_6H_6]{(II)} \underset{70-90\%}{ROSiMe_3}} \ .$$

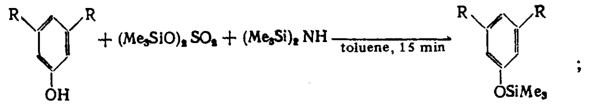
The silyl esters of inorganic acids are sometimes used as silylating agents: silyl perchlorates[13] and bis(trimethylsilyl) sulphate.[19]

Silyl perchlorates, for example compound (III), are obtained from chlorosilane and silver perchlorate[19] and are used to introduce bulky protecting groups [di(t-butyl)methylsilyl groups]:[81]



They are also used as highly selective reagents for the removal of t-butoxycarbonyl groups from peptides.[82]

Bis(trimethylsilyl) sulphate, which is used to silylate OH- and/or NH-containing biologically active compounds, is usually employed in combination with hexamethyldisilazane or *N*-dialkylaminotrimethylsilane:[83]



$\mathrm{R = t\text{-}Bu}$.

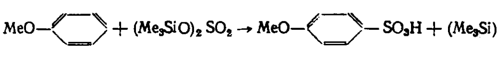
The interaction of bis(trimethylsilyl) sulphate with urea leads to trimethylsilyl isocyanate as a result of the decomposition of the thermally unstable trimethylsilylurea:[84]

$$\mathrm{(Me_3SiO)_2SO_2 + (NH_2)_2CO \xrightarrow[150^\circ]{} Me_3SiNCO + (NH_4)_2SO_4} \ .$$

Silylation of alkali metal nitrates affords trimethylsilyl nitrates:[85]

$$\mathrm{(Me_3SiO)_2SO_2 + KNO_3 \rightarrow \underset{85\%}{Me_3SiONO_2} + K_2SO_4} \ .$$

It is noteworthy that bis(trimethylsilyl) sulphate is also used as a sulphonating agent. Its interaction with aromatic compounds, pyridine, and thiophen leads to the corresponding sulpho-derivatives,[86,87] for example:



The silyl ethers of enols $\mathrm{R_3SiOC{=}C\!<}$ are effective reagents for the silylation of alcohols, carboxylic acids, and certain mercaptans, such as thiophenol:[88–90]

$$\mathrm{\underset{(IV)}{Me_3SiOCR{=}CR'R''} + RXH \rightarrow Me_3SiXR + \underset{86-99\%}{R'R''CHC(O)R}} \ .$$

However, with the aid of silylenols (IV) it is impossible to silylate amides and amines (Schiff bases are formed), ephedrine (oxazolidine is formed), and alkane-thiols (the yield of the trimethylsilyl derivative of 2-mercaptoethanol did not exceed 5%). In addition it has been shown[91] that, in the case of unsaturated alcohols and phenols, another reaction pathway can operate, i.e. the proton donor can add to the double bond of the silylenol:

$$\mathrm{CH_2{=}CHOSiMe_3 + ROH \rightarrow MeCH(OR)OSiMe_3} \ .$$

An analogous result has been obtained also for acids.[92] Despite the limiting applicability of silylenols in the silylation of NH- and SH-containing compounds, they are widely used in organic synthesis.[1,2,19,93,94] The electrophilic reactions of these compounds make it possible to obtain the vast majority of α-functional derivatives of carbonyl compounds. The oxidation and ozonolysis of silylenols lead to α-hydroxy-derivatives.

The reactions of organosilicon ethers of enols (IV) with carbenes lead to the corresponding derivatives of siloxycyclopropane, from which it is possible to obtain in their turn various substituted cyclopropanes and products resulting from the opening or rearrangement of the cyclopropane ring. The $C{=}C{-}OSiR_3$ system participates in the [2 + 2]-, [3 + 2]-, and [4 + 2]-cycloaddition reactions with formation of various cyclic adducts, which are important for the synthesis of biologically active substances.[1] The methods of synthesis of silylenols have been surveyed in a number of reviews.[1,2,19,93,94]

The side reactions accompanying silylation with the aid of silylenols can be avoided by employing the *O*-trimethylsilyl *O*-methyl acetal of methylketen, obtained by the successive interaction of ethyl acetate with lithium diisopropylamide and chlorotrimethylsilane:[95,96]

$$\mathrm{MeCOOEt} \xrightarrow[2)\ \mathrm{Me_3SiCl}]{1)\ \text{iso-}\mathrm{Pr_2NLi}} \mathrm{MeCN{=}C(OMe)OSiMe_3} \xrightarrow[\mathrm{MeCN\ or\ CH_2Cl_2},\ 15\to 40^\circ\mathrm{C}]{\mathrm{RXH}} \underset{95\text{—}99\%}{\mathrm{RXSiMe_3}};$$

$$\mathrm{RXH = PhOH,\ PhCH_2OH,\ 3,4,5\text{-}(MeO)_3C_6H_2COOH,\ PhSH,\ PhCH_2SH,\ \underbrace{C(O)C_6H_4C(O)NH}}\ .$$

The introduction at the oxygen atom of substituents capable of weakening the $(p-d)_\pi$ bonding between the silicon and oxygen atoms and of delocalising the negative charge in the transition state made it possible to obtain a series of new effective silyl donors, among which *N*-alkyl-substituted trimethylsilyl carbamates and trimethylsilyl trifluoromethanesulphonate (trimethylsilyl triflate) are most widely used.

The readily available trimethylsilyl *NN*-dialkylcarbamates exhibit effective silylating properties especially in relation to alcohols, phenols, and acids,[97] the reactions being autocatalytic:[98]

$$\mathrm{R_2NC(O)OSiMe_3 + R'OH \rightarrow \underset{75\text{—}95\%}{R'OSiMe_3} + R_2NH + CO_2};$$

$\mathrm{R = Me;\ R'OH = EtOH,\ t\text{-}C_5H_{11}OH,\ n\text{-}C_7H_{15}OH,}$
$\mathrm{n\text{-}C_{10}H_{21}OH,\ cyclo\text{-}C_6H_{11}OH,\ HO(CH_2)_2OH,}$
$\mathrm{PhOH,\ }m\mathrm{\text{-}MeC_6H_4OH,\ }m\mathrm{\text{-}HOC_6H_4OH,\ }p\mathrm{\text{-}HOC_6H_4OH,}$
$\mathrm{MeCO_2H,\ PhCO_2H.}$

Silyl *NN*-dialkylcarbamates are obtained by passing carbon dioxide through *NN*-dialkylaminotrimethylsilane[99-106] or through a mixture of dialkylamine and hexamethyldisilazane:[107, 108-110]

$$\left.\begin{array}{l}\mathrm{CO_2 + RR'NSiMe_3} \\ \mathrm{CO_2 + RR'NH/(Me_3Si)_2NH}\end{array}\right] \rightarrow \mathrm{RR'NC(O)OSiMe_3}\ .$$

The interaction of silver carbamates with chlorotrimethylsilane also leads to silylated products:[101,111]

$$\mathrm{RR'NC(O)OAg + Me_3SiCl \xrightarrow[-AgCl]{} RR'NC(O)OSiMe_3};$$
$$\mathrm{R = R' = H}\ .$$

According to the authors,[97] the most convenient method of synthesis of *N*-alkyl-substituted trimethylsilyl carbamates consists in the interaction of the adduct of an amine and carbon dioxide with chlorotrimethylsilane:

$$\mathrm{2RR'NH + CO_2 \xrightarrow[CH_2Cl_2]{-10\text{—}0^\circ} [RR'NC(O)O]^- RR'NHH_2^+ \xrightarrow[CH_2Cl_2;-RR'NH\cdot HCl]{Me_3SiCl;0\text{—}20^\circ} \underset{85\text{—}90\%}{RR'NC(O)OSiMe_3}};$$

$$\mathrm{RNH_2 + Et_3N + CO_2 \xrightarrow[CH_2Cl_2]{-10\text{—}0^\circ} [RNHC(O)O]^- Et_3NH^+ \rightarrow}$$
$$\mathrm{\rightarrow \xrightarrow[CH_2Cl_2;\ -2Et_3N\cdot HCl]{2Me_3SiCl/Et_3N;\ 0\text{—}20^\circ} \underset{>70\%}{R(Me_3Si)NC(O)OSiMe_3}}\ .$$

The trimethylsilyl carbamates obtained can be used not only as silylating agents[97,98] but also for the introduction of the amino-group into the molecules of organic compounds, for example:[97]

$$\mathrm{RR'NC(O)OSiMe_3} - \left|\begin{array}{l} \xrightarrow[20^\circ,\ 15\ \mathrm{min}]{\mathrm{R''C(O)Cl}} \underset{85\text{—}95\%}{\mathrm{R''C(O)NRR'}} \mathrm{+ CO_2 + Me_3SiCl}\ ; \\ \xrightarrow[80^\circ,\ 2\ \mathrm{h}]{\mathrm{PhSO_2Cl}} \mathrm{RhSO_2NRR' + CO_2 + Me_3SiCl}\ ; \\ \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{(R''CO)_2O}} \underset{90\%}{\mathrm{R''C(O)NRR'}} \mathrm{+ R''C(O)OSiMe_3 + CO_2}\ ; \end{array}\right.$$

$$\mathrm{R'' = Me,\ Ph,\ ClCH_2;\ R,\ R' = Alk}\ .$$

One of the most active silylating agents is trifluoromethylsilyl trifluoromethanesulphonate (TMS triflate).[1,112-114] It is obtained by heating trifluoromethanesulphonic acid with chlorotrimethylsilane with or without a base[115-118] and also by cleaving aryltrimethylsilanes with this acid:[119]

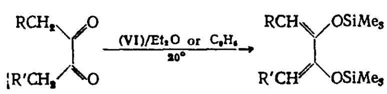
$$\mathrm{CF_3SO_2OH} - \left|\begin{array}{c} \overset{\mathrm{Me_3SiCl}}{\overline{-\mathrm{HCl}}} \\ \underset{-\mathrm{ArH}}{\underline{\mathrm{ArSiMe_3}}} \end{array}\right| \rightarrow \underset{\mathrm{(V)}}{\mathrm{CF_3SO_2OSiMe_3}}\ .$$

Silylation with TMS triflate is usually carried out in the presence of a tertiary amine, triethylamine being the most suitable base, since the salt $\mathrm{CF_3SO_2OH.NEt_3}$ is a liquid; it is insoluble in non-polar solvents and can be readily separated from the easily soluble silylated products. The end of reaction is inferred from the formation of the second phase. Triethylamine is also convenient because it is an effective solvent for weak CH acids. The reaction is usually performed in dichloroethane, since in this solvent the reactions are 10^2–10^3 faster than in $\mathrm{CCl_4}$ or $\mathrm{Et_2O}$.

TMS triflate (V) is most important for the silylation of CH acids.[114]

(1) Ketones and aldehydes[120-124] [by treatment with $\mathrm{CF_3.}$ $\mathrm{.SO_2OSiMe_3/Et_3N}$ (VI)]:

$$\mathrm{RC(O)CHR'R'' \xrightarrow{(VI)} RC(OSiMe_3){=}CR'R''};$$



;

$$\mathrm{RR'CHCHO \xrightarrow[0\text{—}5^\circ]{(VI)/Et_2O} RR'C{=}CH(OSiMe_3)}\ .$$

It has been shown that TMS triflate induces the isomerisation of the *C*-silylation product to the *O*-silylated compound:[124]

$$\mathrm{Me_3SiCH_2C(O)R \xrightarrow[20^\circ,\ min]{(V)/CCl_4} H_2C{=}C(OSiMe_3)R}$$

(2) 1,3-Dicarbonyl compounds:[125]

$$\mathrm{RCH_2C(O)CHR'C(O)R'' \xrightarrow[0^\circ,\ 30\ min]{(VI)} \underset{50\text{—}90\%}{RCH{=}C(OSiMe_3)CR'{=}C(OSiMe_3)R''}}$$

(3) Carboxylic acid esters:[126-128]

$$\mathrm{RCH_2COOR'} \xrightarrow[0\div10^\circ]{\mathrm{(VI)/Et_2O}} \left|\begin{array}{l} \xrightarrow{a} \mathrm{Me_3SiCHRCOOR'}\ ; \\ \xrightarrow{b} \mathrm{RCH{=}C(OR')OSiMe_3}\ ; \\ \xrightarrow{c} \mathrm{RCH_2C(O)OSiMe_3}\ ; \end{array}\right.$$

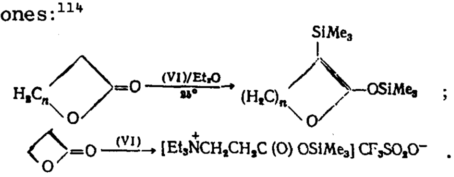
a) R = H, Me, R' = SiMe₃, CH₂Ph, Me, Et, iso-Pr; R=R'=Et; R=SiMe₃, R'=Et, iso-Pr;

b) R=Me, R'=Ph, SiMe₃; R=R'=Et; R=CN, R'=Me, Et; R=SiMe₃, R'=Me, Et, iso-Pr, SiMe₃, Ph; R=CH₂COOEt, Ph, R'=Et ;

c) R' = t-Bu.

The scheme indicates the dominant reaction pathways for various substituents. Thus the product ratio *a*/*b* is 9 : 1 for $\mathrm{CH_3COOPh}$ and 19 : 81 for $\mathrm{CH_3CH_2COOPh}$.[127]

(4) Lactones:[114]

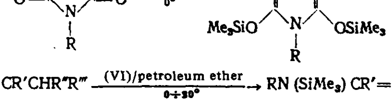


(5) Thiocarboxylic acid esters:[129]

$$\mathrm{RR'CHC(O)SR'' \xrightarrow[0\text{—}20^\circ]{(VI)/CH_2Cl_2} \underset{75\text{—}81\%}{RR'C{=}C(OSiMe_3)SR''}}\ .$$

(6) Amides,[114] imides,[114], imines,[130] and iminoesters:[114]

$$\mathrm{RR'CHC(O)NR''_2 \xrightarrow[0^\circ]{(VI)/CH_2Cl_2} RR'C{=}C(OSiMe_3)NR''_2}\ ;$$



;

$$\mathrm{RN{=}CR'CHR''R''' \xrightarrow[0\div30^\circ]{(VI)/petroleum\ ether} RN(SiMe_3)CR'{=}CR''R'''}\ ;$$

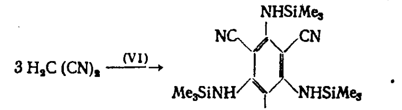
$$\mathrm{MeC(OMe){=}NR \xrightarrow{(VI)} MeC(O)N(SiMe_3)R}\ .$$

(7) Nitriles:[114,131]

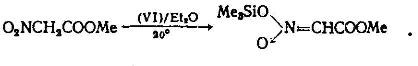
$$\mathrm{RR'CHCN} \xrightarrow{(VI)} \underset{55\%}{\mathrm{RR'C(SiMe_3)CN}} \xrightarrow[R'=H]{(VI)} \underset{33\%}{\mathrm{RC(SiMe_3)_2CN}} \ ;$$

$$\mathrm{RCH_2CN} \xrightarrow[R=Ph]{(VI)} \underset{71\%}{\mathrm{RC(SiMe_3){=}C{=}NSiMe_3}} \ ;$$

$$\mathrm{MeCN} \xrightarrow{(VI)} \mathrm{(Me_3Si)_3CCN + (Me_3Si)_2C{=}C{=}NSiMe_3} \ ;$$



(8) Nitroalkanes:[132]



$$\mathrm{O_2NCH_2COOMe} \xrightarrow[20^\circ]{(VI)/Et_2O} \mathrm{(Me_3SiO)(O^-)N{=}CHCOOMe} \ .$$

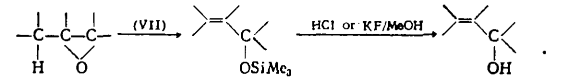
(9) Diazo-compounds:[133]

$$\mathrm{RCHN_2} \xrightarrow[-78^\circ]{(V)/Et_2O} \mathrm{RC(SiMe_3)N_2} \ ;$$

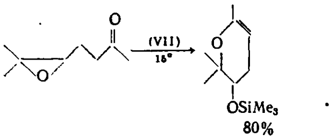
70—82%

$\mathrm{R = P(O)(OR')_2,\ COOR'}$.

Oxirans are silylated by TMS triflate with ring opening,[112,114] which is used widely in preparative chemistry. The reaction proceeds under the influence of CF_3SO_2OSiMe/1,8-diazabicyclo[5.4.0]undec-7-ene (VII):



For example, according to this scheme the following reactions take place:[112,134]

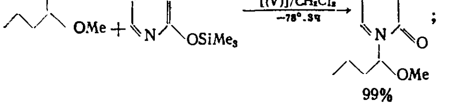


80%

It has been found that tetrahydrofuran (THF) is also cleaved in accordance with this scheme, while ethers do not react with silylated sulphonic acids.

In addition TMS triflate can be used to obtain carbenes.[135]

New methods of organic synthesis involving the employment of TMS triflate as the catalyst of exchange and addition reactions have come to be widely used recently:[112,128,136–140]



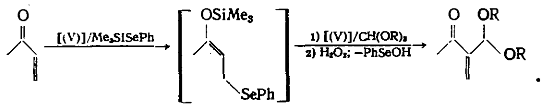
99%

$$\mathrm{Me_3SiOR + R'_3COSiMe_3} \xrightarrow[-(Me_3Si)_2O]{[(V)]} \mathrm{ROCR'_3} \ ;$$

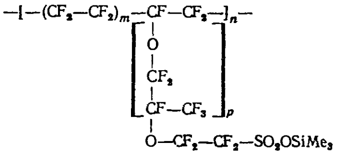
$$\mathrm{R_2C(OR')_2 + Me_3SiR''} \xrightarrow[-MeSiOR']{[(V)]} \mathrm{R_2C(OR')R''} \ ;$$

75—100%

$\mathrm{R'' = H,\ CH_2CH{=}CH_2,\ OCR'''{=}CR'''_2}$;

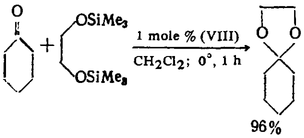


Bearing in mind that in the course of these reactions TMS triflate is lost irreversibly and also taking into account its high relative cost compared with other silylating agents, it has been suggested that TMS triflate be immobilised on a polymer base, which yielded in this way the immobilised catalyst (VIII):[141]



(VIII)

Compound (VIII) can be used both as a catalyst and as a silylating agent,[141] for example:



;

96%

$$\mathrm{EtXH} \xrightarrow[27-29^\circ,\ 2-12\ h]{(VIII)\ or\ (VIII)/Et_3N} \mathrm{EtXSiMe_3} \ ;$$

94—100%

$\mathrm{X = O, S, EtN}$.

Trimethylsilyl trichloroacetate has been recently proposed[142] as a reagent for the silylation of alcohols, phenols, carboxylic acids, amides, acetylenes, and β-ketoesters. The interaction takes place in the presence of potassium carbonate and 18-crown-6 ether on heating for 1–2 h. The chloroform obtained in the reaction promotes the latter:

$$\mathrm{CCl_3COOSiMe_3 + XH \rightarrow XSiMe_3 + CO_2 + CHCl_3} \ ;$$

$\mathrm{X = PhO\,(88\%);\ 3\text{-}MeC_6H_4O\,(90\%);\ PhCO_2\,(88\%);}$

$\mathrm{4\text{-}BrC_6H_4S\,(91\%);\ PhC{\equiv}C\,(88\%)}$ etc.

Trimethylsilyl trichloracetate reacts with aldehydes and ketones to form the silyl ether of trichloromethylmethanol, whose acid hydrolysis affords the free alcohol:

$$\mathrm{RC(O)R' + CCl_3COOSiMe_3} \xrightarrow[100^\circ]{X_2CO_3/18\text{-}crown\text{-}6\text{-}ether} \mathrm{Me_3SiOCR'RCCl_3} \rightarrow$$

$$\xrightarrow{H_3O^+} \mathrm{CCl_3CRR'OH} \ .$$

3. Compounds Containing the Si–N Bond

Compounds containing the Si–N bond are very powerful silylating agents especially for the silylation of OH groups, since in this instance the stronger Si–O bond is formed instead of the comparatively weak Si–N bond. The reaction is also promoted by the protonation of the nitrogen atom of the silyl donor, which decreases or eliminates the $(p-d)_\pi$ interaction between the silicon and nitrogen atoms and facilitates the removal of the leaving group in the form of a neutral molecule.

The most widely used Si–N containing silyl donor is hexamethyldisilazane, which is obtained by the reaction of Me_3SiCl with ammonia[19] (p.128). This reagent is widely employed in the pharmaceutical and chemical industries for the introduction of a temporary protecting group in various organic syntheses and also in chromatography for the modification of the surfaces of solid carriers.

At the same time, hexamethyldisilazane belongs to the group of "mild" silylating agents, i.e. it can be used even with very acid proton donors such as alcohols and phenols. Heating or the presence of a catalyst are necessary for the completion of the reaction. Inorganic acids, ammonium salts, sodium bisulphate, and chlorotrimethylsilane are used as catalysts.[14] The silylation method, the essential feature of which is the employment of an equimolar $(Me_3Si)_2NH/Me_3SiCl$ mixture, proved to be extremely fruitful.[143] This procedure made it possible to intensity appreciably the silylation reaction with the aid of hexamethyldisilazane, to increase the yield, and to reduce the reaction time. The role of $(Me_3Si)_2NH$

then consists in accepting the hydrogen chloride and in generating chlorotrimethylsilane:[144–147]

$$ROH + Me_3SiCl \rightarrow ROSiMe_3 + HCl\ ;$$
$$HCl + (Me_3Si)_2NH \rightarrow Me_3SiCl + NH_4Cl\ \cdot$$

Apart from the intensification process, it has been possible to expand greatly the synthetic possibilities of this reaction, extending it to classes of compounds (such as, for example, mercaptans and siloxanols) whose silylation by both Me_3SiCl and $(Me_3Si)_2NH$ (each separately) is relatively ineffective.[143–147]

Compounds containing the $\equiv Si-\underset{|}{N}-C\ (O)$ group (silylureas and silylamides) are more active silylating agents than silazanes and silylamines.[14,17] Although the majority of trimethylsilylureas can function as effective silyl donors, two representatives of this class have come to be most widely used recently: *NN'*-bis(trimethylsilyl)urea and *NN'*-diphenyl-*N*-trimethylsilylureas. The main advantage of the disilylated urea consists in the ease of its synthesis from widely distributed cheap starting materials: urea and hexamethyldisilazane.[148] The interaction of *N*- and *NN'*-substituted ureas with hexamethyldisilazane leads to isocyanates as a result of the thermal decomposition of unstable reaction intermediates. For this reason, silylureas are synthesised by the reaction of metallated ureas with chlorotrimethylsilane, of *N*-alkyl(aryl)ureas with *NO*-bis(trimethylsilyl)-acetamide, and of organoaminosilanes and organosilazanes with organic isocyanates,[149] which reduces their availability and increases their cost compared with *NN'*-bis(trimethylsilyl)ureas.

NN'-Bis(trimethylsilyl)urea is a convenient reagent for the silylation of alcohols and carboxylic acids.[150] The interaction is usually carried out in methylene chloride for 2–3 h, which ensures a high yield of the silylated derivatives (84 to 96%):

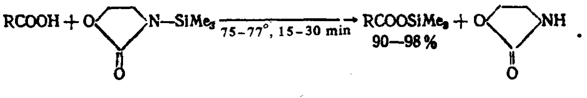
$$ROH + (Me_3SiNH)_2C{=}O \xrightarrow[20-40^\circ]{CH_2Cl_2} ROSiMe_3 + (H_2N)_2C{=}O\ ;$$
$$R = C_9H_{19},\ cyclo\text{-}C_6H_{11},\ p\text{-}MeC_6H_4,\ p\text{-}ClC_6H_4;$$
$$R'COOH + (Me_3SiNH)_2C{=}O \xrightarrow[40^\circ]{CH_2Cl_2} R'COOSiMe_3 + (H_2N)_2C{=}O\ ;$$
$$R' = Ph,\ C_5H_{11},\ ClCH_2,\ H_2C{=}C\ (Me),\ MeCH\ (OH),\ HOOCCH{=}CH{-}\ .$$

NN'-Diphenyl-*N*-trimethylsilylureas, which silylates not only alcohols and acids but also nitromethane, malononitrile, thiourea, guanidine, β-diketones, oxindole, *NN'*-dialkylurea, and other compounds, is a more effective silyl donor.[151] *NN'*-Diphenyl-*N*-trimethylsilylurea is more reactive not only compared with other silylureas but also compared with silyl donors such as *N*-silylamines and hexamethyldisilazane. For example,[151] its interaction with *NN'*-dimethylurea leads to a 100% yield of the silylated product only 2 min after mixing the initial compounds, in silylation with the aid of *N*-trimethylsilylaniline the product is formed in only 3% yield after 3 h, while in the reaction involving *N*-trimethylsilylpiperidine the yield is 10% after 3 days. The reaction with hexamethyldisilazane does not take place at all.

Trimethylsilyl derivatives of diphenylurea are obtained by the reaction of *N*-trimethylsilylaniline with phenyl isocyanate.[151] This compound is a convenient silylating agent, because diphenylurea formed in the reaction is insoluble in most organic solvents and can be readily removed from the reaction mixture by filtration. The insolubility of diphenylurea is apparently the reason why the silyl–proton exchange equilibrium is in this case almost wholly displaced to the right:

$$\underset{}{Me_3SiN\ (Ph)\ C\ (O)\ NHPh + (H_2N)_2C{=}S \xrightarrow[30-35^\circ,\ 2\ h]{MeCN} \underset{82\%}{(Me_3SiNH)_2C{=}S} + (PhNH)_2CO\ .}$$

In many instances *N*-trimethylsilyl-2-oxazolidinone[152] or silylated hydantoins [153,154] are conveniently used for the silylation of carboxylic acids and certain biologically active compounds (penicillins, steroids, etc.):



However, the commonest silylating agents containing the $N-C(O)$ group are silylamides: *NO*-bis(trimethylsilyl)-acetamide,[155] *NO*-bis(trimethylsilyl)trifluoroacetamide,[156] *N*-methyl-*N*-trimethylsilyltrifluoroacetamide,[157] and *N*-(t-butyldimethylsilyl)-*N*-methyltrifluoroacetamide.[158] The reaction of the corresponding amide with chlorotrimethylsilane in triethylamines constitutes a preparative method for the synthesis of the above silylamides, for example:[159,160]

$$RC\ (O)\ NH_2 + 2Me_3SiCl + 2Et_3N \xrightarrow[-2Et_3N.HCl]{t_b,\ 8-15\ h} \underset{\sim 80\%}{RC\ (OSiMe_3){=}NSiMe_3}\ .$$

Another method of synthesis of *NO*-bis(trimethylsilyl)amide is provided by the reaction of carboxylic acid halides with sodium bis(trimethylsilyl)amide:[161]

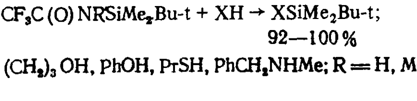
$$RC\ (O)\ Cl + NaN\ (SiMe_3)_2 \xrightarrow[-NaCl]{} RC\ (OSiMe_3){=}NSiMe_3\ ;$$
$$R = Ph,\ C_5H_4N,\ t\text{-}Bu\ .$$

NO-Bis(trimethylsilyl)amides belong to the class of the strongest silyl donors. Alcohols, acids, phenols, amines, mercaptans, amides, ureas, enols, CH acids etc. are silylated with their acid. The silylation is usually carried out in a solvent (benzene, ether, CCl_4, $CHCl_3$, acetonitrile, pyridine, and DMF), which is taken in threefold excess relative to the mass of the initial reactants.[162] Comparison of the silylating properties of *N*-(t-butyldimethylsilyl)-*N*-methyltrifluoroacetamides with those of the t-$BuMe_2SiCl$/imidazole/DMF system showed that the given silylamide is more effective as the silyl donor[163] and the reaction proceeds in acetonitrile at 20 °C:

$$CF_3C\ (O)\ NRSiMe_2Bu\text{-}t + XH \rightarrow \underset{92-100\%}{XSiMe_2Bu\text{-}t};$$
$$XH = HO\ (CH_2)_3\ OH,\ PhOH,\ PrSH,\ PhCH_2NHMe;\ R = H,\ Me\ .$$

For the analysis of organic derivatives by gas–liquid chromatography (GLC), it is more convenient to silylate them by fluorinated silylamides, since fluorinated derivatives are more volatile compared with their non-fluorinated analogues.[14,157]

It has been shown[164] that in the presence of carbon dioxide the silylation of thiazoles by hexamethyldisilazane is accelerated by a factor of 2–3, probably owing to the formation of *NO*-bis(trimethylsilyl) carbamate. It has been suggested that this compound be used as a silylating agent.[101] It can also be synthesised by silylating carbamic acid or its silver salt with chlorotrimethylsilane:



The interaction of the resulting silyl donor with alcohols and acids takes place on heating for 1–2 h and the yield of silylated derivatives reaches 96%:

$$Me_3SiNHCOOSiMe_3 + HX \rightarrow Me_3SiX + CO_2 + NH_3\ ;$$
$$HX = MeOH\ (95\%);\ MeCOOH\ (91\%)\ .$$

NO-Bis(trimethylsilyl) sulphamate has a structure similar to that of the bis(silyl) carbamate and is obtained by means of analogous reactions:[165–170]

$$\left.\begin{array}{l} NH_2SO_3NH_4 + (Me_3Si)_2NH \xrightarrow[-NH_3]{} \\ NH_2SO_3Ag + Me_3SiCl \xrightarrow[-AgCl]{} \end{array}\right] \to Me_3SiNHSO_2OSiMe_3\ .$$

However, *NO*-bis(trimethylsilyl) sulphamate is a much more powerful silyl donor than the bis(silyl) carbamate and many common silylating agents such as hexamethyldisilazane, *N*-trimethylsilyldiethylamine, *N*-trimethylsilylimidazole, and *NO*-bis(trimethylsilyl)acetamide.[167] Alcohols, phenols, acids, organosilicon compounds, and biologically active substances have been silylated with the aid of *NO*-bis(trimethylsilyl) sulphamate.[168–170] Excellent yields (in excess of 90%) of the trimethylsilyl derivatives were obtained in all cases after 30 min at 30 °C. The sulphamic acid liberated as a result of the reaction is insoluble in most organic solvents and can be readily removed by filtration:

$$\underset{93\%}{BuOH + Me_3SiNHSO_2OSiMe_3 \to BuOSiMe_3} + H_2NSO_3H\ .$$

4. Compounds Containing the Si–S Bond

Since the Si–S bond is weaker (63 kcal mol^{-1}) than the Si–O (108 kcal mol^{-1}) and Si–N (77 kcal mol^{-1}) bonds and is more readily polarisable, it is evident that thiosilanes should be more reactive in relation to proton donors than the corresponding oxygen- and nitrogen-containing organosilicon reagents.

Alkylthiosilanes are readily obtained by the reaction of chlorotrimethylsilane with alkylthiomagnesium iodide[19] or with dialkyl disulphide and sodium in ether.[171] However, their reaction with proton donors leads to the evolution of toxic merceptans with an unpleasant smell, which are in addition not always indifferent to the reaction products. These factors limit the application of alkylthiosilanes as silyl donors.

Among the compounds containing the Si–S bond, hexamethyldisilthiane meets the requirements imposed on silylating agents to the greatest extent. It can be obtained from chlorotrimethylsilane and sodium sulphide at 250 °C or by passing chlorotrimethylsilane vapour through a melt of the eutectic mixture of lithium and potassium chlorides containing 25% of potassium sulphide at 400 °C.[19] Hexamethyldisilthiane is also formed when hydrogen sulphide is silylated by chlorotrimethylsilane in the presence of tertiary amines,[19,172] organosilylamines,[19] including *N*-trimethylsilylimidazole,[19] hexamethyldisilazane,[173–175] *N*-phenyl-*N*-silylacetamide,[176] and cyanotrimethylsilane[177] and by the interaction of iodotrimethylsilane with silver[172] and mercury[172,178,179] sulphides.

The reaction of chlorotrimethylsilane with ammonium hydrogen sulphide is an extremely effective method of synthesis of hexamethyldisilthiane:[180]

$$Me_3SiCl + NH_4SH \to (Me_3Si)_2S + NH_4Cl + H_2S\ .$$

However, the easiest and most promising method of synthesis of hexamethyldisilthiane involves the cothiolysis of *N*-trimethylsilyldiethylamine or hexamethyldisilazane with chlorotrimethylsilane:[181,182]

$$Me_3SiNEt_2 + Me_3SiCl + H_2S \to (Me_3Si)_2S + Et_2NH{\cdot}HCl\ ;$$
$$(Me_3Si)_2NH + Me_3SiCl + H_2S \to (Me_3Si)_2S + NH_4Cl\ .$$

The reaction takes place with a small exothermic effect at 20–50 °C in a neutral solvent or without a solvent. The hexamethyldisilthiane formed in this process is 99.95% pure according to GLC data.

Hexamethyldisilthiane is a highly effective reagent for the silylation of alcohols,[19,183–191] aminoalcohols,[187] phosphorylated alcohols,[192] phenols,[194–195] inorganic and carboxylic acids,[194,195,197,198] enols,[199,200] arylmercaptans,[199,200] oximes,[199,200] and also certain organoelemental compounds,[199,201] including organosilicon[202] and organophosphorus compounds:[199,201]

$$(Me_3Si)_2S + 2RXH \to 2Me_3SiXR + H_2S\ ;$$
$$RXH = AlkOH,\ ArOH,\ HO(CH_2)_nOH,\ H_3BO_3,\ H_2SO_4,$$
$$HHal,\ H_2N(CH_2)_nOH,\ ArSH,\ R'C(O)CH_2C(O)R'',\ R'R''{=}NOH,$$
$$Ph_2Si(OH)_2,\ (RO)_2POOH\ \text{etc.}$$

One of the main advantages of hexamethyldisilthiane compared with other silyl donors is the simplicity of the silylation reaction, which is achieved by mixing and heating the initial reactants (at 30–120 °C) for a short time (0.5–3 h), ensuring a high yield (70–98%) of the silyl derivatives. The course of the reaction can be conveniently followed volumetrically from the amount of hydrogen sulphide formed. The reaction does not require the use of catalysts and solvents. Furthermore, hexamethyldisilthiane ensures the selective silylation of proton donors containing two and more active groups in the molecule.[199]

5. Compounds Containing Si–C Bonds

Reagents with the Si–C bond are much more resistant to the action of proton donors than the silyl donors with the Si–Hal, Si–O, Si–N, and Si–S bonds examined above. However, in the presence of catalysts certain compounds containing electron-accepting groups such as C_6F_5, CN, etc. can act as effective silyl donors. Thus, in the presence of strong acids (toluene-*p*-sulphonic[203] or trifluoromethanesulphonic[204] acids), allylsilane silylates alcohols and acids in accordance with the following scheme:

$$CH_2{=}CHCH_2SiMe_3 + ROH \xrightarrow[MeCN]{TosOH} \underset{87\text{—}99\%}{ROSiMe_3} + CH_2{=}CHMe\ .$$

The catalytic action of the above acids consist in the ready cleavage by the latter of the silicon–allyl bond with the intermediate formation of powerful silyl donors—the trimethylsilyl esters of sulphonic acids.[205] Further interaction of these intermediates with proton donors leads to silylated products with regeneration of the acid:[204]

$$CH_2{=}CHCH_2SiMe_3 + CF_3SO_2OH \xrightarrow[20-25^\circ]{CH_2Cl_2} CF_3SO_2OSiMe_3 + CH_2{=}CHMe\ ;$$
$$CF_3SO_2OSiMe_3 + RCO_2H \to RCO_2SiMe_3 + CF_3SO_2OH\ .$$

In the presence of $Bu_4N.3H_2O$ as the catalyst, alkyl trimethylsilylacetates can be used to silylate compounds containing a comparatively acid hydrogen atom, for example:[206]

$$Me_3SiCH_2COOR + XH \to \underset{88\text{—}92\%}{Me_3SiX} + MeCOOR\ ;$$
$$R = Me, Et;\ X = Ph(CH_2)_3O,\ Ph(\text{isoferrocene})_2CO,\ 4\text{-}MeC_6H_4O,\ Me(CH_2)_5S,$$
$$PhCH_2S,\ 1\text{-menthyloxy},\ Me_3CS,\ PhC{\equiv}C,\ EtCOO\ ;$$
$$Me_3SiCH_2COOMe + HO(CH_2)_2SH \to \underset{83\%}{Me_3SiO(CH_2)_2SSiMe_3} + MeCOOMe\ .$$

When the silicon atom is linked to the trichloromethyl group, the cleavage of this bond can take place also in the absence of the catalyst, for example:[207–209]

$$Me_3SiCCl_3 + Bu_2NH \xrightarrow[3-4\ h]{120-140^\circ} \underset{85\%}{Me_3SiNBu_2} + CHCl_3\ .$$

The use of (trichloromethyl)trimethylsilane is convenient also because chloroform formed as a side product can serve simultaneously as the solvent for the reaction product.

(Trichloromethyl)trimethylsilane can be obtained by the reaction of phosphorus acid amides with chlorotrimethylsilane in the presence of CCl_4 [210] and by the decarboxylation of the trimethylsilyl ester of trichloroacetic acid in the presence of triethylamine:[211]

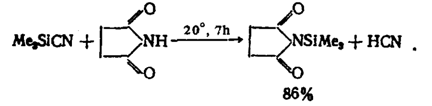
$$(R_2N)_3P + CCl_4 + Me_3SiCl \xrightarrow[Et_2O]{} (R_2N)_3PCl_2 + Me_3SiCCl_3 \ ;$$

$$CCl_3COOSiMe_3 \xrightarrow[66°,\ 4h]{Et_3N,\ THF} \underset{79\%}{Me_3SiCCl_3} + CO_2 \ .$$

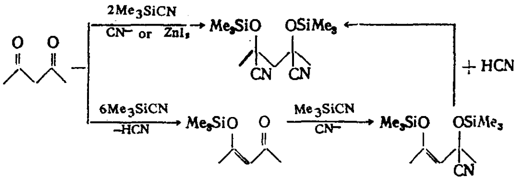
In recent years there has been a growth of interest in cyanotrimethylsilane not only as a reagent which makes it possible to introduce the cyano-group readily into the molecules of organic and organoelemental compounds[1,2] but also as a silyl donor. It has been found[177] that Me_3SiCN readily reacts with compounds containing SH and NH bonds:

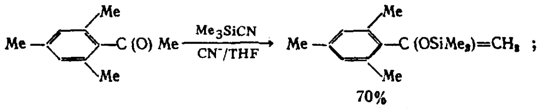
$$Me_3SiCN + H_2S \xrightarrow[80°;\ 3{,}5h]{} \underset{86\%}{(Me_3Si)_2S} + HCN \ ;$$

$$Me_3SiCN + 2Et_2NH \xrightarrow[20°,\ 2h]{} Me_3SiNEt_2 + Et_2NH{\cdot}HCN \ ;$$



The interaction of Me_3SiCN with carbonyl compounds is unusual; depending on the conditions and the catalyst, both silylation and addition to the carbonyl group can take place:[212–215]

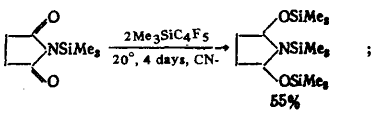


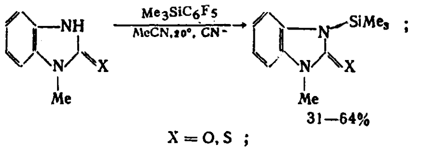


CN⁻ = KCN/18-crown-6-ether.

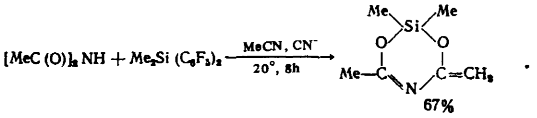
Thus cyanotrimethylsilane can be used to convert a ketone into a cyanohydrin with the simultaneous protection of the hydroxy-group, which has been used in the synthesis of prostaglandin.[2,216]

The successful selection of the catalyst for the silylation of carbonyl compounds (KCN/18-crown-6 ether) made it possible to employ also (pentafluorophenyl)trimethylsilane as the silyl donor. This resulted in the formation of silyl derivatives which are either difficult or impossible to obtain by another method, for example:[212,215,217–222]





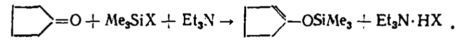
X = O, S ;



III. COMPARATIVE CHARACTERISTICS OF SILYLATING AGENTS

Evidently factors weakening the Si–X bond in the silyl donor R_3SiX increase the rate of silylation. The effect of various factors, including the nature of the leaving group X, the substituents R, the acidity of the proton donor, and the influence of the medium and the catalyst on the efficiency of the silylation, have been described in reviews,[14–24] silyl donors of one class being usually compared. Studies in which a quantitative comparison has been made of the silylating agents with Si–X bonds of different character are more important.

The activity of silyl donors is determined either by measuring the rate of reaction of various silyl donors with the relatively inactive proton donor or the yield of the product of the silylation of this proton donor after a specific time interval is determined. For example, the activities of silyl donors of the type Me_3SiX, where X = Cl, $MeSO_3$, $4\text{-}MeC_6.H_4SO_3$, $PbSO_3$, Me_3SiOSO_3, $4\text{-}BrC_6H_4SO_3$, $CF_3CH_2SO_3$, Br, CF_3SO_3, or I, in relation to cyclopentanone and diisopropyl ketone, have been investigatea.[223] The reactions proceed in the presence of triethylamine in accordance with the following mechanism:



The rate of reaction was determined by ^1H NMR. The extremum values of the standardised rate constants (at 23 °C) and the relative rate constants for the given silylation reactions were calculated. The silylating activity scale was obtained in this way (the reactivity of Me_3SiCl was adopted as unity); the highest reactivity is shown by Me_3SiI:[223]

X	Cl	$MeSO_3$	$PhSO_3$	Me_3SiOSO_3	Br	CF_3SO_3	I
k_{rel}	1	40	160	270	$7{,}9\cdot10^4$	$6{,}7\cdot10^8$	$7\cdot10^9$

In another study[167] the authors claim that *NO*-bis(trimethylsilyl) sulphamate is more effective as a silylating agent than the majority of silyl donors. To confirm this, they compared the efficiency of the most frequently used silylating agents in relation to the silylation with sterically hindered 2,6-di-s-butylphenol; the yield of the silylated product was determined by GLC.

In another investigation[199] the interaction of dodecyl alcohol with a series of silyl donors [chlorotrimethylsilane, hexamethyldisilazane, the equimolar mixture of chlorotrimethylsilane and hexamethyldisilazane, *N*-trimethylsilyldiethylamine, *NO*-bis(trimethylsilyl)acetamide, and hexamethyldisilthiane] was chosen as the model reaction. It was shown by GLC that the reactivities of *NO*-bis(trimethylsilyl)acetamide and hexamethyldisilthiane in relation to the above alcohol are approximately the same and exceed appreciably the reactivities of the remaining silyl donors.

The available data permit the conclusion that the most active silyl donors are trimethylsilyl trifluoromethanesulphonate, iodotrimethylsilane, *NO*-bis(trimethylsilyl) sulphamate, *NO*-bis(trimethylsilyl)acetamide, and *NO*-bis(trimethylsilyl)trifluoroacetamide. Hexamethyldisilthiane and *N*-trimethylsilylimidazole are extremely active in relation to compounds containing OH groups; on the other hand, they are less suitable for silylation of NH and SH bonds.

In recent years there has been a growth of interest in catalytic silylation of proton donors by compounds containing the Si–C bond, although this method has not so far come to be sufficiently widely used.

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Thus, efforts to create new silylating agents or to apply known reagents to silylation have been made in five directions: (1) the synthesis of silyl donors containing groups which would promote easier elimination of the silyl group (trimethylsilyl triflate and trifluoromethyl-containing amides); (2) the synthesis of silyl donors which do not form deposits, during the silylation process, hindering the isolation and purification of silylated products (hexamethyldisilthiane and silyl carbamates); (3) the synthesis of reagents forming in the course of the reaction substances which are indifferent to the reaction products and which liquefy the reaction mass, promoting a higher degree of completion of the process [trimethylsilyl trichloroacetate, alkyl trimethylsilylacetate, (trichloromethyl)trimethylsilane]; (4) the use of catalytic systems which convert known reagents into effective silyl donors (allyltrimethylsilane, hexamethyldisiloxane in the presence of the KCN/18-crown-6 ether complex); (5) the use of reagents which serve simultaneously for the introduction of protecting (silyl) groups as well as other reactive groups (cyanotrimethylsilane). We suggest that the synthetic possibilities of the first two procedures have been virtually exhausted and the main effort will therefore probably be concentrated on the last three procedures, especially that involving the creation of catalytic silylation systems.

In conclusion one should note that the usefulness of a particular silyl donor is determined both by the nature of the compound silylated and by the aim of the investigator. For example, analytical chemistry (GLC, mass spectroscopy) requires highly effective reagents such as trimethylsilyl trifluoromethanesulphonate, which silylate rapidly and quantitatively, although they are usually expensive and scarce. Since the analytical chemist deals with small amounts of substances to be analysed the cost of the silyl donor does not play a significant role for his purposes. On the other hand, in the development of the technology for the large-scale synthesis of organic substances, it is more useful to select a cheaper, albeit a less active silyl donor, such as organochlorosilane or hexamethyldisilazane. In selecting a suitable silylating agent, the synthetic chemist must take into account primarily the structure of the proton donor and the synthetic possibilities of the different silyl donors, information about which is available in monographs,[1,14] original articles,[15–24] and in the present review.

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Polymeric Reagents in the Synthesis of Peptides

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The essential features of the method of polymeric reagents in relation to peptide synthesis are described. The polymer-activators have been classified in terms of the type of activating groups. The procedures used in the synthesis of polymer-activators and polymeric reagents are given and the principal aspects of the employment of the method of polymeric reagents in the synthesis of peptides of various structure as well as the trends and prospects for the development of the method are discussed.

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I. INTRODUCTION

The application of polymers in organic syntheses, and biotechnology has vigorously increased in recent times. For example, recently published monographs[1–7] have been devoted to these questions. Thus the employment of polymers as various supports, in particular for the immobilisation of enzymes[1,3,7,8] and the cells of micro-organisms[1,9–11] and for the affinity chromatography of proteins[5,12,13] is well known. Studies are being prosecuted in order to synthesise polymeric therapeutic agents,[1,14–16] in particular, artificial antigens[17] and synthetic models of enzymes.[3,18,19] Polymeric catalysts[2,20,21] and high-molecular-weight protecting groups are widely used.[2,22] However, the most vigorously developing field is that involving the application of polymers as chemical reagents.[2,4,24,25] The main advantage of this approach is associated primarily with an increase of the yields and the facilitation of the purification of the desired product; in many cases the specificity of the reactions carried out is greatly increased. The application of polymers in multistage monotonic operations, for example, in the synthesis of polypeptides,[26,27] polynucleotides,[28] polysaccharides,[29] and polycondensation polymers with exactly specified numbers of units[30] proved to be especially valuable. Polymers can serve under these conditions as separators of the reacting groups, imitating the conditions of high dilution. The reduction to a minimum of competing intermolecular† interactions makes it possible to employ this principle effectively for the synthesis of cyclic peptides,[7,31] macrocyclic compounds,[32] asymmetric ketones and α-substituted carboxylic acids,[33–35] the Dieckmann cyclisation,[36] the conversion of bifunctional compounds into the monoblocked form,[37,38] etc. The direction of the reaction and the selectivity can change significantly on passing from the usual low-molecular-weight reagents to polymeric reagents.[39,40]

Polymeric reagents are finding useful applications in virtually all fields of organic synthesis. In peptide synthesis the tendency has arisen to refer to polymers which fulfil acylating functions as polymeric reagents.[27,42–46]

The methods of synthesis of polymeric reagents, the use of the latter in peptide synthesis, and the trends and prospects in the development of this approach are discussed in the present review.

II. THE ESSENTIAL FEATURES OF THE METHOD OF POLYMERIC REAGENTS IN RELATION TO PEPTIDE SYNTHESIS

The search for new approaches to the synthesis of biologically active compounds which are protein in nature occupies a special place among the problems of peptide chemistry. "Classical" peptide chemistry, which deals with reactions in solution, has encountered many problems difficult to solve, which include the reduction of the yields with increase in the size of the peptide synthesised, the difficulty of isolating the desired product in a homogeneous state as a consequence of the occurrence of side reactions, and the reduction of the solubility of peptides with increase in the length of their chain.

In the attempts to overcome these difficulties, new ideas have appeared, which are associated mainly with the employment of synthetic polymers. At the beginning of the 1960's Merrifield[26,50] suggested that insoluble polymers be used as carriers of the peptide chain, serving at the same time as the C-terminal protecting group. It then became possible to use a large excess of the activated low-molecular-weight component, whose separation together with soluble side products can be readily achieved by the filtration of the peptide—polymer complex. This "solid phase" method of synthesis gained wide popularity, which was promoted to an appreciable extent by studies on its mechanisation and automation.[51,52] However, in the course of the development of this method, some disadvantages also appeared,[53,54] being associated mainly with the difficulty of eliminating the insoluble side products, accumulated in the course of the synthesis, from the final products.

If a soluble polymer is used as the C-terminal protecting group of the growing peptide, it is possible to diminish the influence of diffusion factors on the course of the reaction. This is the so called "liquid phase" method[55] of peptide synthesis. An obstacle to the wide-scale employment of the liquid phase method, especially in the synthesis of higher

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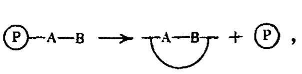
† The term "intrapolymer" reactions is also used for such systems.[41]

peptides, is apparently the difficulty of purifying the reaction product owing to the similarity of the solubilities and molecular weights of the polymer and the peptide synthesised.

In the middle 1960's a methodologically new trend arose, also associated with the employment of polymers but this time as activators of the carboxy-groups of aminoacids or peptides.[27,56] In the general case the covalent polymer–low-molecular-weight reagent complex, which has the free energy necessary for the occurrence of the reaction, effects the transfer of activated groups to the molecules of the other reactant present in solution (reaction (1)]. Here one can also include the reactions between groups present in the polymer phase, i.e. intramolecular (or intrapolymer) interactions [reaction (2)]. Polymeric reagents of the types indicated are also referred to as polymeric transferring agents.[42]

$$\textcircled{\text{P}}\text{—A} + \text{B} \longrightarrow \text{A—B} + \textcircled{\text{P}}\ , \qquad (1)$$



$\textcircled{\text{P}}$ - polymer-activator. (2)

Polymeric condensing agents[43] fit the above definition because the reaction takes place via an intermediate stage—the activation of component A:

$$\textcircled{\text{P}} + \text{A} + \text{B} \longrightarrow \textcircled{\text{P}}\text{—A} + \text{B} \longrightarrow \text{A—B} + \textcircled{\text{P}}\ .$$

In peptide synthesis component A is usually an *N*-substituted aminoacid, whose carboxy-group must be activated before the formation of the peptide bond. Component B is an aminoacid or a peptide with a free N-terminal amino-group. The polymer-activator carries electron-accepting groups for the generation of the positive charge on the carbonyl carbon atom of the aminoacid sufficient for effective attack by the nucleophile. In classical peptide chemistry, activated esters, anhydrides, imides, etc. are usually employed for this purpose.[47–49] In order to accelerate the aminolysis and to ensure that it goes to completion, an excess of the polymeric reagent, which is separated in the last stage of the synthesis, is used as a rule.

The physicochemical properties of the polymer play a very important role both in the synthesis and in the isolation of the product. It is possible to formulate certain general requirements which must be met by polymeric reagents: (1) the polymeric skeleton must be readily permeable to the peptide molecules over a wide range of molecular weights. In the case of polymers of the gel type, the latter must exhibit a satisfactory swellability in the solvents employed; (2) the physical properties of the polymeric species must ensure their ready separation by filtration from the soluble products and their mechanical and osmotic stabilities must be satisfactory; (3) polymeric derivatives of aminoacids must be highly reactive and resistant to racemisation; (4) polymeric reagents must be stable on storage also to the solvolytic action of solvents; (5) polymers must not absorb the soluble components; (6) it is desirable that the polymeric components should be capable of being used many times, i.e. that there should be a possibility of their regeneration without reducing their initial capacity and reactivity and without changing the physicochemical parameters of the polymer.

Among the polymeric reagents used at the present time, polymeric activated esters are most often employed for peptide synthesis:

$$\text{Z—NH—CHR}'\text{COOH} + \text{HX}\textcircled{\text{P}} \longrightarrow \text{Z—NHCHR}'\text{—CO}\sim\text{X}\textcircled{\text{P}} \xrightarrow{\text{H(NHCHRCO)}_n\text{NHCHRCOO—Y}}$$

$$\longrightarrow \text{Z—NH—CHR}'\text{CO(NHCHR)}_n\text{NHCHRCOOY} + \text{HX}\textcircled{\text{P}}\ ;$$

$\textcircled{\text{P}}$ = polymeric skeleton; X = activating group;
Y, Z = *N*- and *C*-protecting groups; $n = 0, 1, 2...$

The condensation of *N*-protecting aminoacids with a polymer-activator leads to the activation of the carboxy-group. The polymeric reagent obtained is introduced into the aminolysis reaction with the corresponding derivative of the aminoacid or peptide containing a free amino-group. The reaction product passes to the solution. After the removal of the *N*-protecting group, the resulting peptide can be made to react again with a second activated aminoacid, effecting thereby the growth of the peptide chain. An important factor in the synthesis of a polymeric aminoacid derivative is the absence of insoluble side products which might contaminate the required product in subsequent aminolysis.

III. SYNTHESIS OF POLYMER-ACTIVATORS

There exist various ways of introducing activating groups into the polymeric skeleton. In some cases the initial polymer is subjected to a series of chemical transformations, while in others a molecule with the functional group already present is attached to a suitable polymeric carrier. The functional group can also be introduced by copolymerising the corresponding monomers or by the ionic binding of the "functional" compound to a strong ion-exchange resin.

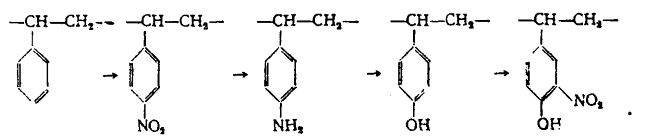
In the vast majority of studies, high-molecular-weight nitrophenols and polymers with the *N*-hydroxy-group are most successfully used for the activation of *N*-protected aminoacids.

There exists at the present time a fairly extensive literature on high-molecular-weight phenols[57,58] of different structure, whose nitration is potentially capable of ensuring the formation of the required nitrophenol polymer-activator. However, in peptide synthesis the higher requirements which must be met by the physicochemical properties of the polymer significantly restrict the choice of such polymers. For example, the widely familiar phenol-formaldehyde resins of the "resite" and "novolak" types[59] are apparently relatively unsuitable for such purposes owing to the difficulties arising in the regulation of the steric structure, the content of functional groups, and the physical shape of the polymer particles. There exist brief reports about the use of such polymers,[56,60] but experimental data on their application are virtually lacking. Amorphous powdered polymers of this type have been obtained by the polycondensation of di(4-hydroxyphenyl) sulphone with formaldehyde[61] or of salicylic acid with anisole and formaldehyde.[62] Many phenol-formaldehyde polymers have also been used in the solid phase synthesis.[31,63–65] The yields of peptides when such a resin was employed were appreciably lower compared with a hydroxylated polymer having a polystyrene skeleton. This effect has been attributed by the authors to steric hindrance—the methylene bridges were located next to the functional groups.

In one of the first studies on the use of polymeric reagents in peptide synthesis,[27] it was suggested that one should use poly-4-hydroxy-3-nitrostyrene, obtained by the hydrolysis of the copolymer of p-acetoxystyrene with 4% of divinylbenzene and subsequent nitration with concentrated acid at 0 °C.[66] This polymer was used successfully in the synthesis of low-molecular-weight model peptides bradykinin and luliberin,[67] but in the course of its application disadvantages were revealed—the decomposition of the polymeric species during the aminolysis reaction and mechanical manipulations which might have led to the contamination of the desired products.[68,69]

Williams[70] suggested that poly-*o*-nitrophenol be synthesised by the block copolymerisation of *p*-methoxystyrene with divinylbenzene, subsequent elimination of the methyl group using boron tribromide and then nitration. The effectiveness of the acylation by *N*-protected aminoacids of both the given polymer and the preceding one[27] was approximately the same (1–1.5 mmol per gramme of polymer).

A similar polymer-activator was obtained in accordance with the following scheme using polymer-analogue reactions:[56]

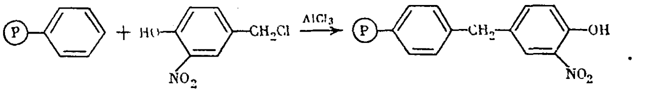


The content of reactive hydroxy-groups was 0.05–0.5 mmol per gramme of polymer, while their theoretical content was 5–7 mmol g^{-1}. Evidently the above scheme is relatively unsuitable for the synthesis of the activator owing to the occurrence of side processes leading to a sharp reduction of the reactivity of the polymer.

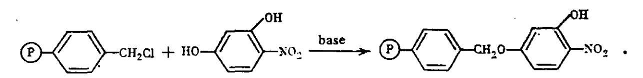
An insoluble phenolic polymer in the form of spherical grains has been obtained.[71] The authors used the copolymerisation in suspension of *p*-acetoxystyrene with styrene and divinylbenzene and the acetate group was split off by hydrazinolysis under mild conditions.

With one exception,[71] in the cases examined the polymers consisted of particles of irregular shape, which was bound to hinder their use owing to cracking and mechanical wear. The occurrence of side reactions in the synthesis of certain polymer entails, together with a decrease of the content of functional groups, also significant changes in the steric structure, for example, owing to additional cross-linking. In order to eliminate the above negative phenomena, it was suggested[72] that the complete functional group be introduced into the polymer-carrier with the required set of physical properties. The authors synthesised a polymeric *o*-nitrophenol using as the carrier spherical grains of a copolymer of styrene with 2% of divinylbenzene, which has found extensive application in the solid phase synthesis of peptides in view of satisfactory physicochemical parameters.

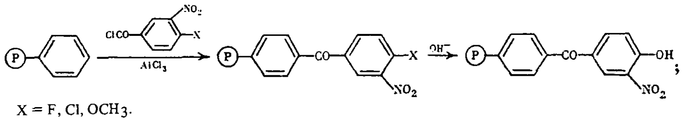
An analogous approach has been used by other workers,[69] who modified the styrene grains with 4-hydroxy-3-nitrobenzyl chloride by means of the Friedel–Crafts reaction:



A polymer-activator of similar structure has been obtained by means of the following scheme:[68]

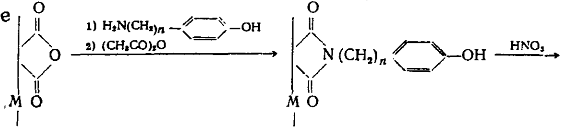


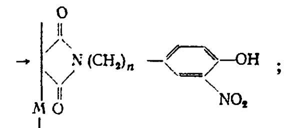
Finally, a polymeric 4-hydroxy-3-nitrobenzophenone has been proposed quite recently for acyl-activation in peptide synthesis:[73]



X = F, Cl, OCH_3.

Low-molecular-weight activated ethers of 4-hydroxy-3-nitrobenzophenone proved to be 40 times more reactive than the corresponding *o*-nitrophenyl ethers. A polymeric *o*-nitrophenol has been synthesised in the laboratory of the authors of the review on the basis of a cross-linked copolymer of styrene with maleic anhydride[74] and of ethylene with maleic anhydride





$n = 0, 1, 2$

$M = CH_2CH_2$ or $CH_2CH(C_6H_5)$.

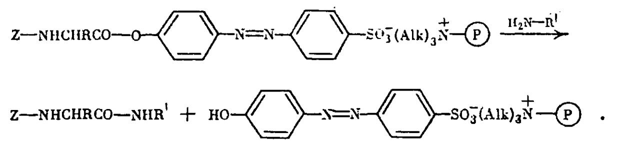
The polymer-carrier consists of spherical grains obtained by cross-linking the initial linear copolymers by aromatic diamines (3–5 mole %) in an emulsion system.[75] Their modification by aminophenols with subsequent nitration led to poly-4-hydroxy-3-nitrophenylmaleimides with a degree of conversion close to 100%.

Practically the same polymer-activator has been obtained by Japanese investigators,[76] who also synthesised a soluble polymeric nitrophenol. However, the method of synthesis of cross-linked polymers differed from that given above;[74] the authors[76] copolymerised *p*-acetoxyphenylmaleimide with styrene in the presence of divinylbenzene with subsequent elimination of the acetyl group and nitration. Both the polymeric mononitro-derivative and the dinitro-derivative—poly-4-hydroxy-3,5-dinitrophenylmaleimide—were obtained.

The polymer-activators obtained by a procedure involving the attachment of a complete activating group to the polymer-carrier were distinguished by a high mechanical strength and swellability in organic solvents of different polarity: in dimethylformamide (DMF), dioxan, methylene chloride, etc. One cannot rule out the possibility that such polymers exhibit a smaller steric effect on the aminolysis reaction, because the reaction centre in the polymeric activated ester is remote from the polymer chain.

A soluble polymer-activator with a nitrophenol group has been obtained[27] from a copolymer of DL-lysine and L-tyrosine[77] and, whilst being insoluble in solvents of low polarity, it dissolves satisfactorily in DMF, ethanol, and water at basic pH. However, this polymer has been used only for the cyclisation of linear peptides.[27] A soluble polynitrophenol obtained from poly(ethylene glycol) is also known;[78] it has been used in the synthesis of model dipeptides.[79]

Mention should be made of a study[80] where the reagent was used in the form of an electrostatic complex:

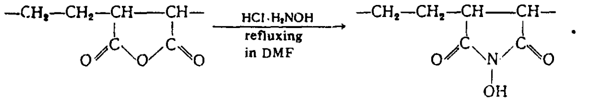


The activated ester of an *N*-protected aminoacid and 4-hydroxyazobenzene-4-sulphonic acid was attached to an ion-exchange resin (Dowex 1X2) by salt formation.[81,82] The aminolysis of the insoluble ester obtained in this way was carried out in formamide. The relatively high swellability of this polymer in highly polar media should favour the use of free aminoacids and peptides as the amino-components. The advantage of this approach consists in the fact that the activated ester was synthesised in solution and it could therefore be purified before being attached to the polymer. A disadvantage of the reagent is the risk of ion exchange and the consequent contamination of the aminolysis products. An acetylated insoluble polystyrene ion exchanger has been proposed[83] for the synthesis of the amide bond in an aqueous medium. However, under the conditions indicated, the acylation of aniline was insufficiently effective—the yield of acetanilide did not exceed 26%.

Attempts have been made to use polymeric thiophenols in peptide synthesis.[56,84,85] Among these, only poly-*o*-nitrothiophenol[85] and poly-2-mercaptopyridine[85] have been used in the synthesis of two peptides, the reagents based on the mercaptopyridine being more reactive (the yield in the condensation reaction was 90–98%). Poly-2-mercaptopyridine also proved an effective thiolytic agent—it has been used for this purpose in order to eliminate the Nps# protecting group at intermediate stages in the synthesis of leucine-enkephalin.[85]

The *O*-acylation of *N*-substituted hydroxylamines attracted much attention by investigators, because the activated esters of this type are highly reactive and are resistant to racemisation.[48] *N*-Hydroxysuccinimide esters[86] derived from *N*-hydroxybenzotriazole[87] have gained much popularity in the classical peptide synthesis and benzotriazole has been frequently used as the catalyst in peptide formation reactions.[88] These particular derivatives have served as prototypes of polymeric reagents with an *N*-hydroxy-group.

A linear copolymer of ethylene with *N*-hydroxymaleimide has been synthesised as follows:[89]

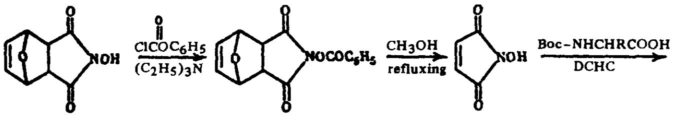


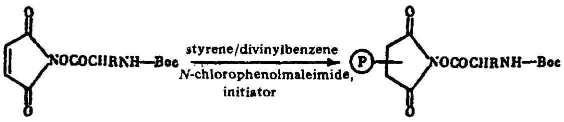
This polymer and its *O*-acyl derivatives dissolved only in polar solvents—DMF and dimethyl sulphoxide (DMSO). For this reason aminoacids were activated by this polymer in the above solvents and the resulting esters were subjected to aminolysis in dimethoxyethane or ethyl acetate in which the polymer does not dissolve. Despite the satisfactory results obtained in the synthesis of low-molecular-weight peptides, its application is limited because many peptides dissolve only in the same solvents as the given polymer. For this reason, the authors apparently used subsequently in the synthesis of higher peptides (from hexa- to octa-peptides) a highly cross-linked polymer, which was obtained by irradiating the above poly-*N*-hydroxysuccinimide with high-energy electrons.[89] The content of active hydroxy-groups then fell to 2%, i.e. the polymer virtually "worked" only in the surface layer.

In contrast to the previous workers,[89] Japanese investigators proposed different methods for the introduction of *N*-hydroxy-groups into the polymer, involving the treatment of the styrene–maleic anhydride copolymer in pyridine under milder conditions—at room temperature.[90–94] The polymer was obtained in the form of a colourless powder with an *N*-hydroxy-group content close to theoretical.[90] It was used for the acetylation and benzoylation of certain amines in a homogeneous system; it was not employed for peptide synthesis.

It has been suggested that *O*-substituted maleimides can be used for the synthesis of cross-linked spherically granulated poly-*N*-hydroxysuccinimides, provided that they are subjected to emulsion copolymerisation with styrene and divinylbenzene.[91] However, spherical grains could not be obtained under the conditions indicated. It is of interest that the maleamic acid (an aminoacid) units present in the polymer chain were readily converted into a five-membered imide ring by dehydrocondensation on treatment with aqueous hydrochloric acid,[90,91] while dehydrating agents or heat were required for the low-molecular-weight analogues.

A novel method of synthesis of the polymeric reagent has been proposed by Akiyama et al.[94]:





Boc = t-butoxycarbonyl
DCHC = dicyclohexylcarbodiimide .

According to the authors' idea, this procedure guaranteed a higher purity of the polymeric activated esters. On the other hand, the introduction of chlorophenylmaleimide into the polymer chain entailed smaller changes in the swellability of the polymer and the solvent was altered during aminolysis.

The copolymerisation of benzyloxymaleimide (or acetoxymaleimide) with styrene and 0.6% of divinylbenzene followed by acid elimination of the *O*-protecting group led to a polymer containing 3–3.5 mmol g^{-1} of *N*-hydroxy-groups.[93]

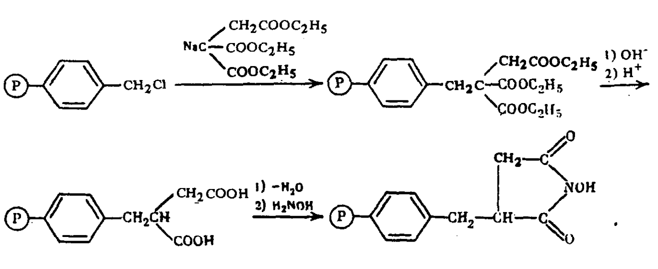
However, it is evident that the schemes for the synthesis of polymeric *N*-hydroxysuccinimides providing for the use of *O*-substituted maleimides are fairly cumbersome and require the expenditure of much time; the synthesis of the initial monomer does not take place with a high yield in all the stages. Furthermore, in the polymerisation of optically active monomers, one cannot rule out the possibility of racemisation, because the process is carried out at an elevated temperature (Akiyama et al.[94] used only simple aliphatic aminoacids).

A simpler and rapid method of synthesis of poly-*N*-hydroxysuccinimide involves the copolymerisation of maleic anhydride with a vinyl monomer (usually styrene) in the presence of divinylbenzene and subsequent modification of the anhydride groups. The introduction of *N*-hydroxy-groups by treating the anhydride polymer with hydroxylamine hydrochloride in boiling DMF has been described,[95] the degree of conversion reaching 88%. Such polymers swell satisfactorily in solvents with a high dielectric constant.

A polymer with an analogous functional group has been obtained by treating the soluble copolymer of ethylene and maleic anhydride with a mixture of hydroxylamine and a polyamine as the cross-linking agent (hydrazine, spermine, and spermidine) in an aqueous pyridine medium. The polymer was distinguished by a high permeability to large molecules, which is indicated by the high yield in the peptide formation reactions and by the quantitative acylation of the terminal amino-groups of insulin.[96]

All the polymer-activators of the *N*-hydroxysuccinimide type examined consisted outwardly of amorphous powders. Repeated use of these polymers is difficult, since the polymer particles of irregular shape are rapidly comminuted, which impairs their capacity for filtration in the swollen state.[96] It is therefore not surprising that only one publication has been devoted to each polymer.

A scheme for the synthesis of the polymer-activator, in which a cross-linked chloromethylated polystyrene in the form of spherical grains is subjected to a series of chemical transformations, has been presented in a review article:[43]

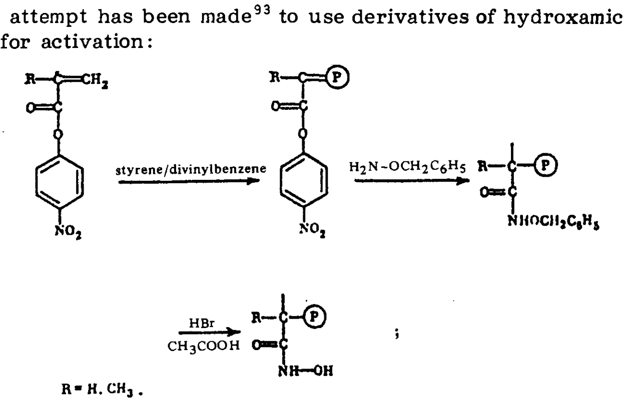


#o-Nitrophenylsulphenyl (Ed.of Translation).

Cross-linked copolymers of maleic anhydride in the form of grains having a regular spherical shape have been obtained by Soviet workers[75,97–100] by cross-linking the initial copolymers by aromatic diamines with a rigid extended molecular structure [benzidine, di(aminophenyl), ether, etc.] in DMF dispersed in a liquid polysiloxane. *N*-Hydroxy-groups were introduced by treating the anhydride polymer with hydroxylamine hydrochloride in pyridine; their content in the final polymers reached about 4 mmol per gramme of the polymer. The grains of all the poly-*N*-hydroxysuccinimides obtained swelled satisfactorily in polar organic solvents, while the polymers into the composition of which *N*-vinylpyrrolidone has been introduced[97–100] also swelled satisfactorily in an aqueous medium. The particles of the polymeric *N*-hydroxysuccinimide had a satisfactory mechanical strength and osmotic stability and were easily filtered in the swollen state. The acylation of the hydroxy-groups in the polymer was almost quantitative.[97–102] These polymers have a macronetwork isoporous skeleton[103] and it has been shown[104] that polymers with this structure are satisfactorily permeable to large molecules.

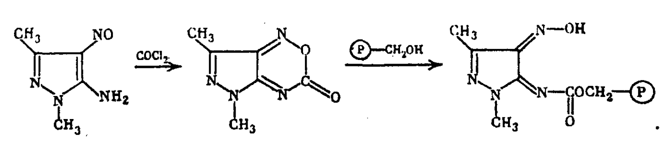
As can be seen, there exists a fairly large selection of methods for the synthesis of polymeric *N*-hydroxysuccinimides. Evidently, the simplest and cheapest versions are those which begin with copolymers of maleic anhydride. One should bear in mind that such copolymers contain rigorously alternating units[105,106] and that by selecting the appropriate comonomers it is possible to alter significantly some of their properties, for example their hydrophilic/hydrophobic properties,[98,100] and the microenvironment of the reaction centre.[94]

An attempt has been made[93] to use derivatives of hydroxamic acid for activation:



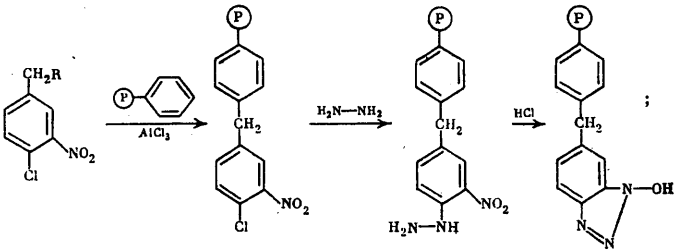
In the case of a polymer containing acrylic acid residues, the above reactions occurred with a higher yield than for a copolymer of methacrylic acid. The attempt to copolymerise methacryloylhydroxylamine acid with styrene was unsuccessful.[93] The aminolysis of O-acyl derivatives of the resulting polymer (R = H) by certain aliphatic aminoacids and amines led to fairly low yields of amides, which can be attributed to the low reactivity of this polymeric reagent[107] and steric hindrance.

Guarneri et al.[108] suggested that a polymeric derivative of 5-amino-4-nitrosopyrazole be used as the activator:



It had been shown earlier that low-molecular-weight activated esters based on 5-aminopyrazolone oxime exhibit a very high acylating capacity in the virtual absence of racemisation.[109] An interesting feature of this oxime is that, by virtue of the presence of conjugated double bonds, it is coloured green, while its *O*-acyl form is red, as a result of which it is possible to follow visually the occurrence of aminolysis. The amount of the *N*-protected aminoacids applied to the polymer (condensation with the aid of DCCD) was 0.25–1 mmol g^{-1}. The introduction of aminoacids with a bulky side group into the polymer involves certain difficulties.

Among the activated esters known at the present time, the acyl derivatives of *N*-hydroxybenzotriazole are some of the most powerful acylating agents[88] and the *N*-hydroxy-derivative itself effectively accelerates the aminolysis reactions of other activated esters[88] and is frequently used in combination with dicyclohexyl carbodiimide (DCCD) for the condensation of peptide fragments in order to reduce the extent of racemisation. An insoluble polyhydroxybenzotriazole has been obtained in accordance with the following scheme:[110]

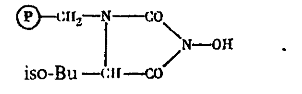


A macroporous spherically granulated copolymer of styrene with 2% of divinylbenzene (XE-305), alkylated with a chloronitrobenzyl derivative by the Friedel–Crafts reaction, was used as the carrier. Best results were obtained when a substituted benzyl alcohol (R = OH) was employed. Further treatment of the resulting derivative with hydrazine in boiling methylcellosolve with subsequent dehydration by boiling concentrated HCl afforded a polymer-substituted *N*-hydroxybenzotriazole (up to 1.4 mmol g^{-1} [111]). The polymer swelled satisfactorily in DMF and methylene chloride and reactions involving it occurred extremely rapidly. The authors[111] regard this support as almost ideal for the method of polymeric reagents in peptide synthesis.

It has been shown[73] that the reactivity of polymeric derivatives of *N*-hydroxybenzotriazole is higher than that of the corresponding derivative of o-nitrophenol by a factor of 100, while that of the low-molecular-weight analogue is higher by a factor of 8000. This difference has been attributed to the low rate of mass transfer within the polymer pores.[73]

When a soluble polymeric form of *N*-hydroxybenzotriazole was used,[78,79] no effect of the polymeric activating group on the rate of aminolysis was noted. However, it has been concluded[79] that such soluble polyoxyethylene-bound reagents are useful only in the synthesis of peptides which are satisfactorily soluble (only in this case is the separation of the polymer from the peptide at the end of the reaction sufficiently complete—by precipitation, recrystallisation, or ultrafiltration).

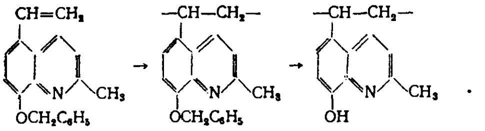
There are apparently definite prospects for the development of new polymer-activators based on substituted hydroxylamines. For example, it has been shown[112,113] that the esters of certain *NN*-diacylhydroxylamines and a series of oximes with electron-accepting substituents are highly reactive in aminolysis reactions. There exists also a brief communication[114] about the use of a polymer containing 3-hydroxyhydantoin groups in peptide synthesis:



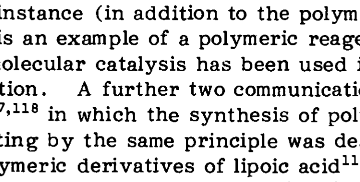
Ⓟ = polystyrene cross-linked with 2% of divinylbenzene

This polymer has been used either to activate Z-Gly in the synthesis of the peptide ZpGly-Ala-OC$_2$H$_5$ or as an additive in the synthesis of the same peptide by the DCHC method. In the second case the yield and optical purity of the products were higher.

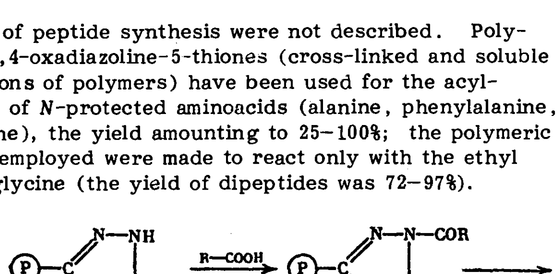
Other types of polymer-activators have been described in the literature. For example, the polymeric analogue of 8-hydroxyquinaldine has been described.[115] It had been used earlier for peptide synthesis in solution.[116] It was obtained by the copolymerisation of 8-benzyloxy-5-vinylquinaldine with 20 mol % of divinylbenzene and subsequent debenzylation with concentrated HCl:



The polymer was tested in the synthesis of a simple dipeptide. The limited amount of data available makes it impossible to assess its advantages, but it apparently possesses no advantages compared with the compounds discussed above. However, this instance (in addition to the polymeric hydroxybenzotriazole) is an example of a polymeric reagent where the effect of intramolecular catalysis has been used in the aminolysis reaction. A further two communications appeared subsequently[117,118] in which the synthesis of polymeric reagents operating by the same principle was described. These were polymeric derivatives of lipoic acid[117] (the coenzyme of acyltransferases) and 1,3,4-oxadiazoline-5-thione.[118] The first derivative[117] was used to activate only *p*-nitrobenzoic acid and the diacyl and not the monoacyl form obtained:



Examples of peptide synthesis were not described. Polymeric 1,3,4-oxadiazoline-5-thiones (cross-linked and soluble modifications of polymers) have been used for the acylactivation of *N*-protected aminoacids (alanine, phenylalanine, and leucine), the yield amounting to 25–100%; the polymeric reagents employed were made to react only with the ethyl ester of glycine (the yield of dipeptides was 72–97%).



It has been suggested that the polymeric reagent based on polyacrylamide with thiol functional groups be used in an aqueous medium for the synthesis of the amide bond.[119] The acylation of this polymer was sufficiently effective, the content of acetyl groups reaching 2.2 mmol per gramme of the polymer. The data on the application of the resulting polythioester in an aqueous medium are discussed in Section V.

An attempt has also been made to use polymeric mixed anhydrides as acylating agents.[68,83] The anhydride of an *N*-protected aminoacid and a sulphonated polystyrene was employed for the acylation of certain simple aminoacids and peptides.[68,83] An analogous reagent has been proposed[120] for the esterification of alcohols; the anhydride of benzoic acid and a carboxylated polymer has been used for the acylation of aromatic amines.[121,122] The employment of such reagents is problematic, because the nucleophilic attack is not always selective—is not directed to the required carbonyl, its direction depending to a large extent on the steric hindrance. The degree of racemisation occurring when this method is employed is greatly influenced by different factors.[123]

IV. POLYMERIC ACTIVATED ESTERS

In the general case the rate of aminolysis depends on the concentration of the reactants. Since the reaction proceeds within the polymer grain, the effective concentration of the carboxy-component (*N*-protected aminoacid) in the polymeric ester should be determined by the content of the component in the dry polymer, the swellability of the polymeric ester, and the accessibility of the reaction centres to the amino-component. The amount of solvent should be sufficient for the complete swelling of the polymer particles and for their suspension in the solution of the amino-component. Since swellability is a constant parameter of the given polymer and solvent, in order to increase the rate of the reaction it is essential to endeavour to achieve the maximum possible content of the activated aminoacids in the polymer. It is noteworthy that in the case of soluble polymers the creation of a high concentration of the carboxy-component is prevented by the increasing viscosity of the polymer solution.

The effect of the application of polymeric reagents in peptide synthesis depends to a large extent on the yields of the aminoacid derivatives and the ease with which they can be introduced into the polymer. For example, in certain studies a large excess (up to a ninefold excess[72]) of expensive amino-derivatives has been used for condensation with the polymer and, if one takes into account the fact that an excess of the carboxy-component is also used in aminolysis, then the useful employment of the aminoacid derivative then amounts to only several per cent.

The degree of acylation of the polymer-activator by *N*-protected aminoacids is determined by many factors—the method of esterification, the nature of the activating groups and their steric environment, the homogeneity of the polymer network, and the structure of the aminoacid. In order to assess the effectiveness of the methods of synthesis of the polymeric esters, one should evidently employ not the content of the aminoacid residues in the polymer but the yields of the carboxy-component introduced into the polymer and the degree of its utilisation. Here one should bear in mind that in most cases the polymer can be regenerated while the isolation of the aminoacid derivatives which have not reacted with the polymer is extremely difficult. For such assessment, it is essential to know the content of the functional groups in the polymer-activator. In certain cases the investigators restrict themselves to elemental analysis, which does not allow inferences about the content of the reactive groups or groups accessible to acylation. The occurrence of side reactions during the synthesis of the polymer-activator and also the slight changes in the architecture of the polymer skeleton can nevertheless influence significantly the effectiveness of the esterification.

An important condition for the synthesis of polymeric esters of any type is a high initial concentration of the reactants in solvents inducing an effective swelling of the polymer. In this sense, DMF, methylene chloride, and their mixtures can be well recommended.[69,101,124]

DCCD has been used as the condensing agent in the activation reaction by most investigators. For polymeric phenols, the method proved to be the most successful.

Condensation via the *p*-nitrophenyl ether or azide[60] methods yielded worse results and has been hardly used. Acylation of the polymers by the Schotten–Baumann method is also relatively unpromising from the standpoint of racemisation.[62,73]

There exist data concerning the use of symmetric anhydrides of *N*-acylaminoacids,[73,78] but best results (81–100%) have been obtained in this instance by employing a soluble polymer-activator[78] and a comparatively large excess (by a factor of 2–4) of symmetrical anhydrides.

It must be emphasised that in the case of polymeric phenols, obtained by the addition of the activating group to the polymer-carrier, a higher degree of acylation has been achieved in contrast to the polymers where the phenol ring enters into the composition of the polymer chain; it approached 100%.[69,72] When the functional group is remote from the polymer chain, more complete condensation is evidently favoured.

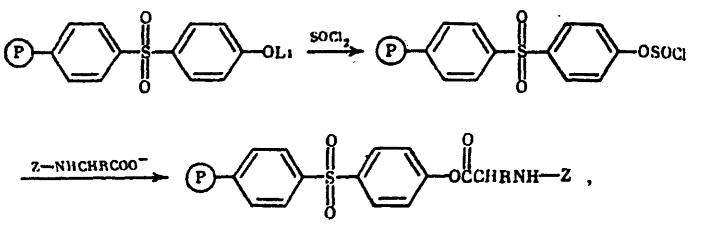
Data have been published[69] on the kinetics of the condensation of benzyloxycarbonyl- and t-butoxycarbonyl-phenylalanine with 4-hydroxy-4-nitrobenzylpolystyrene (cross-linked) in DMF and methylene chloride. It was shown that in the case of the second derivative the rate of reaction was somewhat higher. The solvent did not exert a major influence, some difference being observed only in the initial rates; after 5 h have elapsed, the degree of acylation of both aminoacid derivatives became identical and reached a maximum. In the same study it was noted[69] that the esterification of *N*-protected proline used DCCD was unsatisfactory, the method of mixed anhydride yielding much better results.

DCCD has also been used preferentially for the acylation of polymers with an *N*-hydroxy group; the condensation usually occurred with a satisfactory yield. The difficulties associated with the removal by washing from the polymeric ester of the dicyclohexylurea produced in the course of the reaction must be included among the disadvantages of the DCCD method. A case has been described[43] where, even after repeated washing of the polymer by various solvents, the urea derivative could not be fully eliminated from the polymer. It is apparently undesirable to use DCCD for the introduction of *N*-protected asparagine and glutamine into the polymer in view of the possible formation of nitrile derivatives,[125,126] which may be incorporated into the polymer. A side reaction of DCCD with *N*-hydroxysuccinimide, which can occur also in the polymer, has been described.[127]

The synthesis of polymeric aminoacid esters via mixed anhydrides has certain advantages, because the side products formed are readily soluble in organic solvents. This method has been used to acylate polyphenols,[60,61] poly(5-vinyl-8-quinaldine),[115] and also *N*-hydroxysuccinimide polymers.[89,102,126]

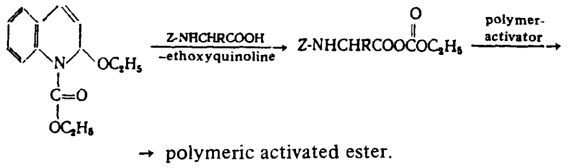
It has been shown[128,129] that high yields of low-molecular-weight *N*-hydroxysuccinimide esters of acyl aminoacids can be obtained in the virtual absence of racemisation if *N*-methylmorpholine is used as the base in the formation reaction of the mixed anhydride. This method has been employed successfully[126] also for the synthesis of polymeric *N*-hydroxysuccinimide esters using DMF and tetrahydrofuran (THF) as the solvents, the polymer being acylated by the mixed anhydride at 40–50 °C. The entire synthesis occupied about 1 h and the yields were 70–90%.

For the condensation of an *N*-protected aminoacid with a polymer having a phenol-formaldehyde structure, the latter was subjected to preliminary activation with $SOCl_2$ or $COCl_2$:[61]



where Z is an *N*-protecting group and R a side group of the aminoacid. For this polymer, the yield in the acylation reaction by the above method was virtually the same as in the carbodiimide and mixed anhydride methods (the aminoacid content in the polymer was 0.9–1.1 mmol g^{-1}).

The method based on the application of *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline can also be included among the mixed anhydride methods:[130]



Although this reagent has been used exclusively for the formation of the amide bond, especially in solid phase synthesis,[131] the authors tested it in the synthesis of polymeric *N*-hydroxysuccinimide esters.[126] It was found that the reaction proceeds fairly slowly (in DMF or THF) and the yields do not exceed 40–50%.

The use of transesterifying agents is one of the most effective methods of synthesis of activated esters.[132] The method involves the acylation of the corresponding hydroxy-component (*N*-hydroxysuccinimide, phenol derivatives) by the anhydride of a strong organic acid (trifluoroacetic, trichloroacetic) with subsequent transesterification of the resulting ester with an *N*-protected aminoacid in the presence of a base in an aprotic solvent. Despite the possibility of the occurrence of side reactions[133] in the transacylation of *N*-trifluoroacetoxysuccinimide with an *N*-acylaminoacid in the presence of a tertiary amine, this method has been used fairly successfully also for the synthesis of polymeric *N*-hydroxysuccinimide esters.[126] It is noteworthy that extremely high yields have been noted in the condensation of acylpeptides by this method, although in the presence of an optically labile *C*-terminal aminoacid there is a possibility of racemisation.[126]

Different types of polymeric activated esters of virtually all natural aminoacids have now been obtained. The benzyloxycarbonyl and t-butoxy carbonyl,[60,89,101] nitrobenzenesulphenyl,[102,124] and trifluoroacetyl[126] groups have been used as N^{α}-protecting groups.

The simplest method for the determination of the content of the activated aminoacid in the polymeric ester is the gravimetric method, which is fairly accurate if the amount of aminoacid applied to the polymer is large (in excess of 0.5 mmol per gramme). In a number of studies[90,91,93,101] the capacity was determined from the yields of the cyclohexylamide derivatives obtained as a result of the interaction of the isolated polymer with an excess of cyclohexylamine. In an alternative version,[69,73] the polymeric ester was treated with a solution of benzylamine in toluene and the excess benzylamine which failed to react was titrated with 0.1 *N* $HClO_4$ in acetic acid using Methyl Violet as the indicator. Aminoacid analysis after the exhaustive hydrolysis of the sample of the polymeric ester with a 1 : 1 mixture of 12 *N* HCl and CH_3COOH has been used in two investigations.[69,124] In one of them,[124] the benzyloxycarbonyl group was determined spectrophotometrically (at 257 nm) after the alkaline hydrolysis of the polymeric nitrophenyl ester of the *N*-protected aminoacid. In certain cases it is possible to use elemental analysis, for example, when the acyl derivative contains sulphur (the Nps group, methionine, or cysteine).[102,124] All the methods indicated yield approximately identical results and one must also bear in mind that in practice a high accuracy in the determination of the capacity of the polymeric reagent is not required because it is as a rule used in excess in the aminolysis reaction. In addition, one may mention that methods for the non-aqueous titration of activated esters have been examined in two communications,[134,135] but these apparently can also be applied to the corresponding polymeric derivatives.

V. SYNTHESIS OF PEPTIDES WITH THE AID OF POLYMERIC REAGENTS

The aminolysis of a polymeric ester, leading to the formation of a peptide bond, proceeds in the solvated polymer—solvent heterogeneous system. The rate of the process should depend on many factors: the nature of the activated ester, the rate of diffusion of the amino-component in the polymer, the accessibility of the reacting group of the polymer, the capacity of the polymeric reagent, and the partition coefficient of the amino-component between the solvent and the swollen polymer, as well as the changes in the swellability of the polymer during the reaction. The reaction kinetics can change significantly as a function of the size of the amino-component, because the rate-limiting stage of the process can change. In one case this is the chemical stage and in another the diffusion stage. In order to reduce the contribution of diffusion factors, the reaction is usually performed in solvents causing a satisfactory swelling of the polymer (extending its polymer network), or when used as carriers which are weakly swelling and have a large surface area and a large pore diameter.[110] In all cases the necessary condition for the successful aminolysis is the solvation of the reaction centres of the polymer. As the reaction proceeds and the polymeric reagent is gradually deacylated, the character of the interaction of the solvent with the polymer can change. This is expressed as a rule by the polymer becoming less hydrophobic and by a change of swellability. For example, in the case of *N*-hydroxysuccinimide hydrophobic polymers, some decrease of swellability was observed during aminolysis[75,101] (in DMF and methylene chloride) or its increase (in water)[97,98]—for hydrophilic poly-*N*-hydroxysuccinimide reagents. The magnitude of this change should depend on the reactant ratio and the capacity of the polymeric reagent. This effect should in its turn influence the permeability and the partition coefficient.

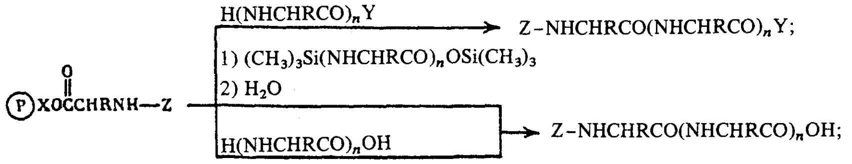
The study of the kinetics of the solid-phase synthesis[136,137] and the aminolysis of polymeric esters[138] showed that the course of such reactions differs significantly from that of reactions in solution. With increase of the degree of reaction, a sharp fall of its rate is usually observed. For example, a study of the rate of aminolysis of polymeric *N*-hydroxysuccinimide esters of Nps-aminoacids[138] showed that the rate constants calculated assuming the first order of the reaction differed at the beginning and at the end of the reaction by 1—3 orders of magnitude. The cause of this difference is apparently the fact that the reacting groups fixed in different compartments of the polymeric species exist under non-equivalent conditions owing to the different microenvironments ("clones" of the reaction centres). This leads to different rates of diffusion of the amino-component to the reaction centres ("microheterotropism"). The swellability of the polymeric reagent, varying in the course of the reaction, may exert an additional influence on the diffusion.

The dependence of the change in the rate of reaction on solvent polarity need not necessarily be correlated with the analogous dependence for reactions in solution, because the change in swellability may have a greater influence on the rate than chemical causes. Thus Kemp[139] found that the reactivity of *N*-hydroxysuccinimide esters in solution decreases in the sequence toluene—methylene chloride—DMF. In the solid phase synthesis the sequence was the same for the *N*-hydroxysuccinimide ester—aminoacyl-polymer (cross-linked polystyrene) system.[137] However, in the aminolysis of polymeric *N*-hydroxysuccinimide esters,[138] the opposite dependence was observed: in DMF the rate of reaction was a maximum and the degree of swelling of the polymer-activator was also greatest in the same solvent.[75,137]

Evidently, as regards the preparative aspect, the application of an excess of the polymeric ester should lead not only to a greater degree of completion of the reaction but should also appreciably improve its kinetic indices, because in this case the most accessible clones of the activated groups of the polymeric esters enter into the reaction while changes in the volume of the polymer are small. A graphical representation of the time variation of the degree of acylation of the methyl ester of leucine by the soluble *p*-nitrophenyl and the polymeric nitrophenyl ester of carbobenzoxyphenylalanine in chloroform in the presence of a twofold excess of the carboxy-component has been published.[69] When the initial concentrations were identical, the curves virtually coincided and the degree of conversion reached 100%.

Comparative estimation of the reactivities of the polymeric reagents is not simple in view of the absence of clear-cut criteria. The yield is in many cases almost quantitative. A "direct" kinetic comparison of two polymeric reagents has been achieved in a study[110] where the degrees of acylation of an alanine ester by t-butoxycarbonylalanine esters were compared as a function of time; the insoluble 4-hydroxy-3-nitrobenzylpolystyrene[69] and *N*-hydroxybenzotriazolylpolystyrene[110] were used as the polymer-activators. The rate of reaction for the first polymer was appreciably lower. The ratio of the reaction half-lives for these polymers was 20 : 1 and the 100% conversion times were 10 and 0.2 h respectively.

With increase of the length of the peptide synthesised, the role of the diffusion factor increases as a result of which the rate of acylation and the yields can decrease significantly. The size of the peptides synthesised hitherto with the aid of polymeric reagents has not exceeded 10 aminoacid residues in the chain. Within these limits, no clear retardation of the reaction or decrease of the yields as the peptide grows have been observed. The nature of the *N*-terminal aminoacid[110] and the character of the activating group[96] played a much more important role than the size of the amino-component. Thus it has been shown[140] that the method of polymeric reagents can be combined fairly successfully with the liquid phase method for the synthesis of peptides. In particular, the reaction involving the condensation of the polyhydroxybenzotriazole ester of t-butoxycarbonylalanine (taken in threefold excess) with the high-molecular-weight component H-Val-O-POE (POE = polyoxyethylene M-6000) during a period of 2 h occurred almost quantitatively; the yield in the analogous reaction with the ester based on polynitrophenol was 30% after 24 h.



X = activating group of the polymer Ⓟ
Z = *N*-protecting group
R, R^1 = side group of aminoacid
Y = OAlk, NH$_2$
n = 1, 2, 3, ...

High-molecular-weight amino-components, namely insulin and poly-ε-benzyloxycarbonyl-L-lysine (M = 10000), have also been acylated with the aid of the poly-*N*-hydroxysuccinimide reagent.[96] Analysis of the reaction products showed that the free amino-groups were almost wholly blocked. Admittedly, a considerable molar excess (50 to 100-fold) of the polymeric t-butoxycarbonylalanine ester was used in the reaction and for this reason one cannot rule out the possibility that the reaction proceeded mainly in the surface layer of the polymer particles.

The majority of the known polymeric reagents swell satisfactorily only in organic solvents and for this reason esters or amides of aminoacids and peptides, which are soluble in these media, were used as the amino-components. The solubility of the intermediate peptide fragments depends not only on their molecular weight but also on the character of the functional side groups and their blocking.[54] When polymeric reagents are used, the set of compatible protecting groups and the strategy used in constructing the peptide chain are essentially the same as in the classical peptide synthesis. However, the problem of the solubility of the growing amino-component is particularly acute in this method owing to the heterogeneity of the reaction system. An increase of its solubility can be achieved only by reducing to a minimum the protecting side groups, which should enhance its hydrophilic properties,[54,140,141] or special protecting groups increasing the affinity of the peptide for organic solvents, both low-molecular-weight[142] and high-molecular-weight,[140] should be used.

The application of free aminoacids and peptides as nucleophiles in combination with organic solvents is limited owing to their low solubility. However, it has been shown[143,144] that, when certain peptides are suspended in a solution of an activated ester in DMSO, the reaction can proceed at an appreciable rate and with a high yield (the equilibrium shifts towards the soluble reaction product in the course of the reaction). The above method has been used to synthesise peptides with the aid of polymeric macronetwork *N*-hydroxysuccinimide esters[101] and model tetra- and penta-peptides as well as a whole series of diastereoisomeric dipeptides have been obtained.[145] The presence of quaternary ammonium bases increases significantly the rate of reaction.[143,145] It is noteworthy that activated esters are not altogether stable in polar organic solvents[144,146] and, since in this case the rate of aminolysis is nevertheless comparatively low and depends on the solubility of the peptide, the method can prove to be unsuitable for the synthesis of complex peptides.

There have been a number of studies[101,147–149] where trimethylsilyl (TMS) derivatives of aminoacids and peptides were used in the reaction with polymeric *N*-hydroxysuccinimide esters. Such derivatives exhibit an increased solubility in aprotic solvents, but they are hydrolytically unstable. The deblocking of the TMS-derivatives is almost instantaneous on treatment with water or alcohol[150] and the TMS group is for this reason suitable as a temporary protecting group for OH, COOH, and in certain cases SH functional groups.[148,151] There exists a fairly large selection of silylating agents at the present time[152,153] and mild methods have been devised for the introduction of the TMS group into aminoacids and peptides.[148] We may note that the amino-group is usually also silylated (although not always[153]), whereupon its nucleophilic properties can be appreciably weakened but the deacylated hydroxy-component evolved in the reaction desilylates it. For this reason, in the case of trifunctional aminoacids entering into the composition of the peptide chain, a stable protecting group is required for the NH$_2$ and SH side groups. For reaction to occur, total silylation of all the functional groups, sufficient to ensure the dissolution of the amino-components, is necessary. If a non-nucleophilic silylating agent is added to the suspension of an insoluble peptide or aminoacid and the activated ester, the equilibrium shifts in the required direction—the aminocomponent is converted into the soluble reactive form. TMS-amides are usually employed as silylating agents.[153,155] However, one should bear in mind that such TMS-amides can themselves interact with the activated esters,[156] i.e. they can initiate competing reactions in the system. This can be avoided if the amino-component is silylated separately and is then introduced into the aminolysis reaction after the removal of the excess of the TMS-agent.

Aminolysis in aqueous and aqueous organic media has definite advantages. Firstly, there is no need for the blocking of the weakly nucleophilic functional groups of the amino-component, secondly, the problem of the solubility of the peptides is in many cases solved, since they usually lose their ability to dissolve in organic solvents as the chain grows, and, thirdly, an aqueous medium at the physiological pH has the least denaturing effect on biologically active compounds. Intense research has been conducted recently on these lines. This concerns the use of enzymes for the formation of the peptide bond, for the introduction and removal of the protecting groups, and in chemical methods of synthesis of the peptide bond. A recently published review has been devoted to the problems enumerated above.[157]

Three types of hydrophilic polymeric reagents, to some extent suitable for the formation of the peptide bond in aqueous media, are known: acylated polymeric sulphonic acid[83] and polymeric thiol[119,158] as well as poly-*N*-hydroxysuccinimide reagents.[97–100]

A mixed anhydride of a polymeric sulphonic acid cation exchange resin and acetic acid[83] has been used in the reaction with aniline in an aqueous medium at pH 3.5–5.5; the low yield of acetanilide (it did not exceed 26%) was explained by the hydrolytic loss of the acylating agent and the low concentration of aniline in the polymer phase (3% relative to the concentration in the external solution).

When an acetylated polymeric thiol[119,158] was used in the aminolysis of amines and aminoacids, best results (yield up to 95%) were achieved at pH 10–12 and the lowest yield of amines was obtained at pH 7.5. This type of dependence is a consequence of the catalysis of the aminolysis by OH^- ions and the positive influence of imidazole $H_2BO_2^-$ and Ag^+ ions was also noted. Best results were also obtained using sterically unhindered amines taken in excess (two equivalents).

In contrast to the polymeric reagents examined above,[83,119,158] which were in fact used only as acetylating agents (for the introduction of the *N*-acetyl group), hydrophilic poly-*N*-hydroxysuccinimide reagents have found practical applications in the synthesis of taftsin,[98,99] 26–33 fragment of cholecystokinin,[98,99] and diastereoisomeric dipeptides.[97] Poly-*N*-hydroxysuccinimide esters of *N*-acylaminoacids exhibited a high reaction capacity (up to 1.8 mmol g^{-1}) and swelled satisfactorily in aqueous media.[99] The rate constants for the competing aminolysis and hydrolysis reactions in heterogeneous system poly-*N*-hydroxysuccinimide reagent–amino-component–aqueous medium have been calculated at different pH for two peptide formation reactions.[159,160] The time variation of the calculated rate constants confirmed the idea of the clonal distribution of the reaction centres.[138] The optimum conditions for the aminolysis were discovered from the kinetic data obtained, in particular the optimum pH was in the region of the p*K* of the amino-group of the amino-component other conditions being equal.

When hydrophilic poly-*N*-hydroxysuccinimide reagents were used to analyse the optical purity of the aminoacids,[97] a polymeric ester of an *N*-protected L-aminoacid was introduced into the reaction with the aminoacid to be analysed, taken in a free form; the aminolysis was carried out at pH 8.5–9.0 (yield 55–98%). The removal of the *N*-protecting (t-butoxycarbonyl) group from the dipeptide obtained was also achieved in an aqueous medium *in situ*. Racemisation and stereoselectivity were not observed when this method was used.

Biologically active peptides—taftsin and the 26–33 fragment of cholecystokinin[98,99]—were synthesised in an aqueous medium at pH 8–9 as a rule under pH-static conditions (arginine was employed in a free state and the hydroxy-groups of tyrosine and threonine were not protected); the 26–33 fragment of cholecystokinin was obtained in an organic solvent (DMF) as a control for the method. The yields in the condensation reaction amounted to 60–86% in both aqueous and organic media.

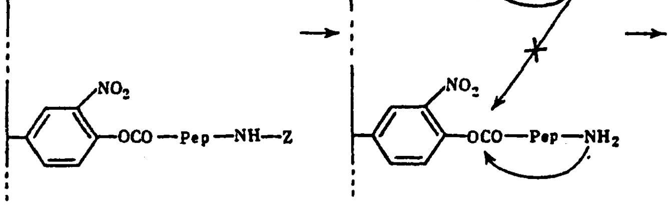
It was noted[98,99] that, when polymeric reagents are used for peptide synthesis in an aqueous medium, there is a possibility of difficulties in the elimination of the hydrolysed carboxy-components from the aminolysis products.

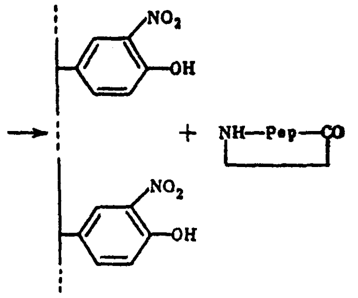
None of the versions of the aminolysis examined above eliminate the necessity for protection also of the functional side group as well as the α-aminogroup in the trifunctional aminoacid in the synthesis of the polymeric activated ester. However, in this case the group may be blocked by protecting groups which are removed simultaneously with the N^{α}-protecting group, for example the *O*-t-Bu group combined with the N^{α}-Boc group. Such a strategy has been used in the synthesis of pentagastrin.[149]

Both in the classical peptide synthesis and in the method of polymeric reagents, the aminolysis can be usually followed qualitatively with the aid of thin-layer chromatography by tracing the disappearance of the amino-component. When polymeric esters containing a chromophoric group in the acyl component are used, there is a possibility of the direct quantitative estimation of the degree of reaction by spectrophotometric measurements on the solution. The kinetics of the aminolysis of polymeric insoluble esters of Nps-aminoacids (λ = 380 nm) [138] and the interaction of the polymeric esters Boc-Ala with the *p*-nitrobenzyl ester of alanine (λ = 280 nm) were investigated in this way.[110] In a study[159] of the kinetics of the aminolysis reaction, the increase of the concentration of the peptide synthesis was followed by studying samples of the supernatant solution with the aid of liquid chromatography after the removal of the *N*-protecting group. Titrimetric determination of the amine which failed to react with the aid of $HClO_4$ in dioxan was used.[69]

In its practical aspect, the method of polymeric reagents has not so far found extensive application in the solution of specific synthetic problems. Peptides synthesised in this way served, with some exceptions, only to test the usefulness of a particular polymer-activator and to develop a methodology. As a rule, all the peptide derivatives were obtained by the stepwise growth of the peptide chain from the C-end. Apart from numerous model peptides, certain natural biologically active compounds and their fragments were obtained. One of the first known peptide hormones—bradykinin Arg-Pro-Pro-Gly-Phe-Ser-Pro-Phe-Arg—has been synthesised with the aid of the nitrophenol polymer[124] in an overall yield of 39% (65.3% relative to the protected nonapeptide) and exhibited the full biological activity. Satisfactory results were obtained in the synthesis of pentadecapeptides using insoluble *N*-hydroxysuccinimide polymers,[89,96,101] 4-hydroxy-3-nitrobenzylpolystyrene,[69,161] and polymeric *N*-hydroxybenzotriazole.[67,84,110,111] Fragments of oxytocin and pentagastrin,[162,163] thyroliberin,[110] the substrates for pig elastase,[164] the pentapeptide fragment of ox carboxypeptidase A,[96] taftsin and its analogues,[98,165] luliberin,[67,166] fragments of ACTH,[161] the *C*-terminal half of α-thymosin,[111] the 26–33 fragment of cholecystokinin,[98] and leucine-enkephalin [84] were synthesised in this way. The use of polymeric *N*-hydroxysuccinimide esters of t-butoxycarbonyl-L-aminoacids proved convenient in the synthesis of the diastereoisomeric dipeptides used in the enantiomeric analysis of aminoacids.[97,145,147,167] The possibility of the repeated employment of the polymeric reagent, the ease of standardising all the mechanical operations, and also their simplicity are significant advantages in routine analysis. Polymeric activated esters have also been used to acylate biogenic and synthetic amines. The high yields and ease of purification of the resulting amides made it possible to employ them successfully in the synthesis of physiologically active aminoacid derivatives of β-phenylethylamine,[168] penicillins and cephalosporins,[166] aminoacyl- and peptidyl-nucleotides,[169] and acylaminophosphonic acid.[170]

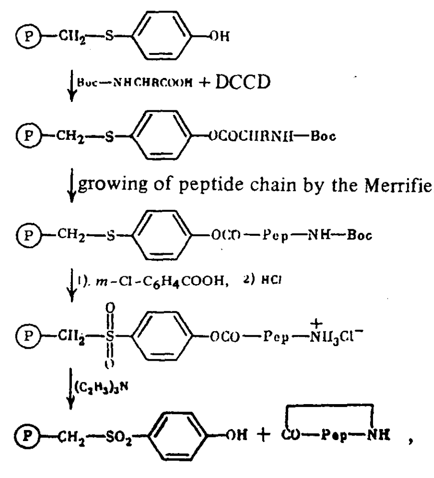
Cyclic peptides are usually obtained by the intramolecular condensation of linear peptides and, in order to suppress the competing intermolecular interactions, the reaction is carried out under the conditions of high dilution.[47] However, as a rule, even under these conditions, an appreciable amount of oligomeric side products is formed. In order to solve this problem, it has been suggested that peptide chains be fixed to an insoluble carrier after which intermolecular aminolysis is to be carried out.[27] The polymer serves in this case as a separator for the peptide chains, so that the unimolecular reaction should become the dominant process. Two versions of the application of monomers for this purpose are possible. In the first version the peptide chain was added to the polymer via a functional side group.[171] In the second version a polymer-activator was used for cyclisation:





Pep = peptide, Z-N = protecting group .

The first stage included the formation of the polymeric activated ester of the *N*-protected peptide. Nitrophenol polymers were used exclusively for this purpose,[27,84] while the condensing agent was DCCD. The yields were fairly low at this stage. However, one should bear in mind that, in order to reduce side reactions to a minimum, the content of acyl residues in the polymer should not be high. In the subsequent stages the *N*-protecting group was removed under acid conditions and the amino-group was deprotonated by an organic base, after which the polymer was maintained in the swollen state for the required time.[27] A series of simple cyclic di-, tri-, and tetra-peptides have been obtained in this way in a yield of 60–80%.[60] In order to obtain cyclic peptides, a linear peptide was initially synthesised by the solid phase method,[31] the ester bond in the peptide-polymer was then activated, and the cyclisation was finally carried out by the method indicated above[27] (yield 40–60%):



where Boc = t-butoxycarbonyl, DCCD = dicyclohexylcarbodiimide, R = side group of the aminoacid, and Pep = peptide.

The "selective activation" principle[§] has been used in a number of other studies for the synthesis of both cyclic and linear peptides.[172–175] The application of oxidants for the labilisation of the peptidyl–polymer bond limits the choice of peptides for the synthesis, because in this case they must not contain a readily oxidisable aminoacid (methionine, cysteine, or tryptophan).

The idea that peptide chains and the reacting groups in the polymer are fully isolated from one another in space and that their interaction is extremely limited has been criticised in a number of investigations.[43,176] Many facts indicated that, even in the case of polymers with a relatively high degree of cross-linking, the internal mobility of the polymeric segments cannot be eliminated.[177]

The question of the influence of the condensation method and of the nature of the polymer-activator on the degree of racemisation of the peptide synthesised has been hardly touched upon in the literature.[178] One should distinguish racemisation proceeding during the activation of the carboxy-component by the polymer-activator and the racemisation in the aminolysis of the activated ester.[139,179] The methods for the formation of the peptide bond have come to be evaluated in this respect by the synthesis and analysis (liquid chromatography[76]) of a "test peptide", where readily racemised acylaminoacids are used as the carboxy-component.[180] The degree of racemisation in the synthesis of the model peptide Z-Gly-L-Ala-L-Leu-OBzl has been estimated[178] (the Izumiya test[181]) by the method of polymeric reagents, which consisted of polymeric esters based on 4-hydroxy-3-nitropolystyrene[27,124] and polymeric *N*-hydroxysuccinimide.[89] The authors compared this with the racemisation occurring when the usual low-molecular-weight condensing agents are employed. Polymeric Z-Gly-L-Ala esters have been obtained with the aid of DCCD and the aminolysis reactions carried out in dimethoxymethane. Diastereoisomeric analysis of the deblocked tripeptide showed that the content of the D-isomer was 6.4% for the *N*-hydroxysuccinimide polymer and 37.4% for the nitrophenol polymer. On the other hand, when DCCD or DCCD with *N*-hydroxysuccinimide were used as condensing agents for the formation of the peptide bond in solution, the amounts of the D-isomer were 24.6 and 2.8% respectively. The data obtained were of the integral type as regards the polymers and the differential estimation of the influence of various factors on the racemisation from experimental data is difficult. The above results[178] are therefore valuable only in the practical sense. It is evident, for example, that the *N*-hydroxysuccinimide polymer is preferable to the nitrophenol polymer from the standpoint of racemisation. When polymer-activated aminoacids with protecting groups of the urethane type are used, the probability of racemisation is minimal, with certain exceptions.[182] For this reason, in most studies where such derivatives were employed, the racemisation was either not estimated during the synthesis or the peptides synthesised were compared with optically pure authentic specimens. Racemisation was not usually observed. This factor made it possible to use the *N*-hydroxysuccinimide polymeric reagents for the enantiomeric analysis of aminoacids.[97,145,147,168]

The attempt to employ the optically active polymeric 3-hydroxyhydroxyhydrantoin for asymmetrically selective peptide synthesis is noteworthy.[114] Two versions of the synthesis of the dipeptide Z-Gly-Ala-OC$_2$H$_5$ from DL-Ala-OC$_2$H$_5$ were achieved in the above study. In the first version the corresponding activated Z-Gly ester was obtained in the preliminary step by the DCCD method and in the second the polymer was used as an additive in condensation by the same method. In the first case the dipeptide obtained contained 54.6% of the L-aminoacid and in the second case 72.6%. This effect was accounted for by the interaction of the D-isomer with the 3-hydroxyhydantoin group in the polymer, which increased the amount of the L-isomer in the solution.

VI. POLYMERIC CONDENSING AGENTS

The use of dehydrating agents makes it possible to simplify greatly the working procedures associated with the formation of the peptide bond. Carbodiimides are usually employed

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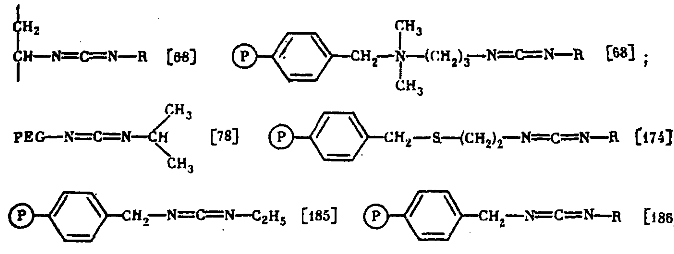
[§] In non-Soviet literature different terms are used for the principle: the "safety-catch principle" [176] and "*a posteriori* activation".[177]

for this purpose.[183] The polymeric reagent with the functional group indicated has been known for a comparatively long time:[184]

$$[-(CH_2)_6-N=C=N-]_n \ ,$$

Data for a series of cross-linked[68,174,185,186] and soluble[78] polymeric carbodiimides having the following structures appeared:



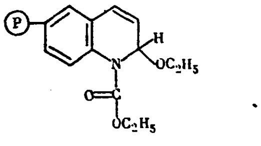
PEG = poly(ethylene glycol), R = alkyl.

For this synthesis, the polymer containing primarily amino-groups was usually treated with the corresponding isocyanate and the resulting polymer-bound urea was dehydrated. Cross-linked polystyrenes have been used as carriers as a rule.

The advantage achieved when such polymers are used may be imagined to consist in a more complete activation of the carboxy-component if the condensing agent is taken in excess and both this agent and its conversion products can be readily removed from the peptide in solution.

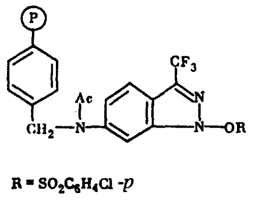
The practical application of classical peptide synthesis and also studies on the kinetics and mechanism of peptide condensation with the aid of DCCD have shown that such reactions have complex mechanisms.[187,188] A side reaction involving the formation of *N*-acylurea, leading to the loss of the carboxy-component, has been frequently observed under these conditions. This side reaction occurred also in the case of a polymeric analogue,[186] which precluded its complete regeneration. The formation of symmetrical anhydrides[188] can also hinder the purification of the final product.

A condensing agent based on polyvinylquinoline[189,190] activates selectively the carboxy-component, converting it into a mixed anhydride of ethoxycarbonic acid:

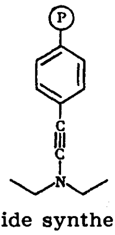


An analogous low-molecular-weight reagent, *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline, had been used earlier in the classical and solid phase methods of synthesis.[130,131]

A further two polymeric condensing agents have been obtained from chloromethylated polystyrene, namely polymer-bound indazole[191] and aynamine:[192]



$R = SO_2C_6H_4Cl\text{-}p$



There is little information about peptide synthesis with the aid of polymeric condensing agents and only several di- and tri-peptides were synthesised in the above studies. Tests for racemisation[189,190] showed that it occurs at the level of low-molecular-weight analogues. The advantages of these reagents became more clearly defined when they were used in other fields of organic synthesis, for example, for the oxidation of alcohols,[193] for the preparation of symmetrical anhydrides[186] and esters, including activated esters.[184]

VII. CONCLUSION

In essence, in any approaches to peptide synthesis one of the reactants is used in excess to ensure the completion of the reaction. The method of polymeric reagents has the advantage that it makes it possible to simplify the purification of the reaction product—the excess polymeric reagent and the deacylated polymer-activator can be readily separated from the low-molecular-weight reactant. In addition, the majority of the known polymer-activators can be used repeatedly, since they are readily regenerated. In particular, the inclusion of the activating components in the polymer makes it involatile and removes its toxicity and unpleasant small. By taking into account the specific features of the microenvironment of the reaction groups and the possibility of modelling high dilution conditions by their separation, it is possible to solve a series of problems which are difficult to solve with the aid of other methods of peptide synthesis.

In the practical application of any method, the prospect of its automation is always attractive. As regards the method of polymeric reagents, the column version of the automation of peptide synthesis has been most frequently forecast.[194] In this case each stage in the formation of the peptide bond requires a separate column with a polymer-activated carboxy-component.

The main purpose of the column is to obtain at the outlet the pure product in a quantitative yield. However, studies in the authors' laboratory[195] showed that a (2-4)-fold excess of poly-*N*-hydroxysuccinimide reagents relative to the amino-component and low rates of elution did not lead to the required required result: the product required additional purification. This is apparently associated with the inadequately high rate of reaction and the absence of fractionation in the case of comparatively low and similar molecular weights of the dissolved components of the reaction mixture. A higher excess of the polymeric reagent in trivial aminolysis reactions is undesirable. Furthermore, the automated method should include a further two stages involving the concentration of the solutions and *N*-deblocking, which are fairly difficult to automate. However, attempts have been made, for example, to employ polymers for the removal of a series of *N*-protecting groups: Nps,[85] Boc,[196] and Fmoc.[197,198] The above considerations apparently complicate the automation of the method of polymeric reagents; virtually no studies on this subject have been described in the literature. A complicating factor is also the fact that industrial manufacture of the polymeric reagents has not so far been initiated, although these are as a rule fairly stable compounds which are convenient to store and transport.

The limits of the applicability of the method of polymeric reagents in relation to the synthesis of high-molecular-weight peptides have not so far been determined. However, it is apparently more most useful to obtain by this method a comparatively small peptide containing 15–20 aminoacid residues (in order to avoid diffusional complications) with subsequent combination of the resulting fragments in solution using either chemical or enzymic methods.

During the preparation of the review for publication, the communication of Patchornik and co-workers appeared in which they describe approaches to the methodology of peptide synthesis using a "mediator" (Mediator Methodology) in a two-polymer system.[199] Also published was a review by the same authors on polymeric transferring agents[200] and polymeric activated esters based on a high-molecular-weight 1-hydroxy-2-pyrrolidinone[201] were proposed.

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Variants of Thin-layer Chromatography with Controlled Flow of the Mobile Phase

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The review is devoted to the methods for controlling the flow of the mobile phase which have been developing successfully in thin-layer chromatography (TLC). Their use makes it possible to eliminate some of the principal disadvantages of the traditional TLC with retention of the majority of its advantages. The continuous variant, the continuous variant with flow type detection, the centrifugal variant of TLC, and also the variant of TLC under pressure are examined. It is shown that control of the flow of the mobile phase makes it possible not only to employ TLC successfully for the selection of separation conditions in column liquid chromatography (CLC) but also to approach CLC as regards performance and speed. At the same time it gives rise to new possibilities for the automation of TLC.
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I. INTRODUCTION

The method of thin-layer chromatography, proposed in 1938 by the Soviet scientists Izmailov and Shraiber,[1] is at present one of the principal procedures in liquid chromatography. It is used in the study of organic[2] and inorganic[3] substances and has found applications in biochemistry and pharmacology,[4,5] in medicine,[6] and in the analysis of the environment,[7] polymers,[8] etc. Such wide-scale application of TLC can be accounted for by the following advantages of this method: (1) the simplicity of the equipment and of the experimental methods, (2) the possibility of altering purposefully and relatively simply a large number of parameters optimising thereby the separation process, (3) economy, (4) the possibility of separating simultaneously and independently a large number of samples in the course of a single determination (up to 20 samples). Important features of TLC such as the possibility of the rapid and simple replacement of the mobile and stationary phases, which determine the selectivity of the method,[4,9-15] and of using the two-dimensional separation technique,[4,9,10,16] which significantly increases the real resolving power of the method must also be specially emphasised. The advantages of TLC include also the fact that on a plate it is possible to analyse all the mixture components and not only those which have reached the detector, as happens in column chromatography.

The commonest variant of liquid chromatography is at the present time column liquid chromatography (CLC) and especially its modern version—high performance liquid chromatography (HPLC). However, the features of TLC mentioned above ensure that it has many advantages over CLC, which have also been responsible for the fairly wide scale employment of TLC in analytical practice. Furthermore, after comparing CLC and TLC, certain investigators give preference to the latter.[17-19] It has been suggested in a review[20] that, although HPLC is superior to high performance TLC (HPTLC) as regards efficiency and the number of components separated, nevertheless the difference between them is not fundamental.

However, compared with HPLC, traditional TLC suffers also from certain disadvantages; (1) a lower reproducibility of the retention parameters, (2) usually a longer separation time, and (3) the existence of certain complicating factors which may have a negative influence on the reproducibility of the chromatographic process (for example, the separation into layers of the solution of the multicomponent mobile phases as they move through the sorption layer,[21] which has been observed in many instances, and the evaporation and adsorption of the vapour of the mobile phase), and (4) a more laborious and complex automation of the entire process—from the introduction of the sample and the preparation of the chromatographic plate up to the quantitative assessment of the results obtained.

The majority of the disadvantages of traditional TLC are associated with the use of a non-stationary virtually uncontrolled flow of the mobile phase (see, for example, Refs. 4, 9, 10, and 22-24). The flow rate of the mobile phase in the layer varies signigicantly during elution and the distance traversed by the front of the mobile phase Z_f is quadratically related to the elution time t:[9,22-25]

$$Z_f^2 = kt \;, \tag{1}$$

where k is the rate constant, which depends on the nature of the mobile and stationary phases.

It follows from Eqn.(1) that the rate of movement of the mobile phase front diminishes appreciably as one moves away from the site where the eluent is supplied. It is also essential to note that the pressure drop caused by capillary forces precludes the achievment of optimum rates of movement of the mobile phase throughout the elution zone. For this reason, elution on most of the plate takes place in traditional TLC at rates below the optimum values.

The non-stationary nature of the flow of the mobile phase, the formation of an unsaturated zone in the region of the eluent near the front, in which the content of the solvent relative to the sorbent differs significantly from the equilibrium value,[9,25-27] and the processes involving the evaporation and adsorption of the components of the mobile phase[28] have an appreciable negative influence on the effectiveness of the separation, the reproducibility of the retention parameters, and the chromatographic process time. A number of studies[29−33] have been devoted to the optimisation of the chromatographic process in TLC, mainly by means of the concerted selection of the sorbent, the mobile phase, and the length of the chromatographic plate. In our view the creation of, firstly, a stationary flow, and, secondly, the optimum flow of the mobile phase, or one approaching the optimum, also plays an important role in the optimisation of the separation process in TLC. The use and development of elution methods which make it possible to obtain a stable flow of the mobile phase (which it is desirable to contol) is one of the promising trends in TLC, because, in combination with the known methods for the optimisation of separation conditions,[29−33] it helps to overcome the principal disadvantages of the traditional TLC, among those enumerated above, retaining at the same time most of its advantages. This is why the present review is devoted to the consideration of methods of TLC with a controlled flow of the mobile phase (TLC-CF).

II. CLASSIFICATION OF TLC METHODS WITH CONTROLLED FLOW OF THE MOBILE PHASE

Variants of TLC in which a stationary flow of the mobile phase, controlled only by employing special methods involving elution and action on the chromatographic system by various physical forces can also be usefully included among TLC-CF methods. Among the variants of TLC-CF known at the present time, it is possible to distinguish two groups: continuous TLC methods and TLC methods with forced flow of the mobile phase. Such subdivision is caused primarily by the difference between the forces responsible for the movement of the mobile phase. In the first group of methods, these are capillary forces. This group includes the continuous combined (two stage), the continuous single-stage (flow), and the continuous TLC methods with a moving attached layer of the sorbent.

In continuous two-stage TLC the sample is deposited on the dry sorbent after which the mobile phase is eluted up to the point where it is removed from the bed under the conditions of the usual TLC with a variable rate of elution (first stage); next, until the end of separation, the rate of elution remains constant (second stage). The rate of elution in the second stage depends on the length of the elution zone, i.e. on the distance between the site where the eluent is supplied and the site where it is removed.

In continuous single-stage TLC the sample is injected directly into the steady flow of the mobile phase. The rate of elution from the instant of the introduction of the sample up to the end of its separation is constant.

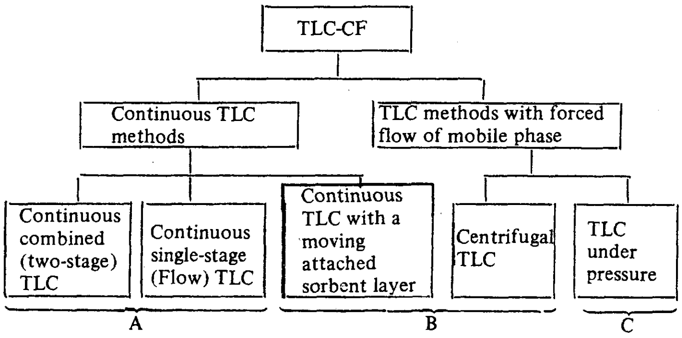
In the third method of this group, the sorbent, attached to a flexible support, moves in the direction opposite to that of the component to be separated. The sample can be deposited on the dry sorbent or can be injected into the flow of the mobile phase.

The term "forced flow TLC" was introduced by Kalász[34] quite recently. It has been used directly to designate the method of TLC under pressure (TLC-P),[35] in which the movement of the mobile phase in the sorbent layer, as in HPLC, is achieved as a result of the excess pressure at the entry of the eluent into the chromatographic system. However, we think that it is more useful to include in the concept of "forced flow TLC" (TLC-FF) all the variants of TLC in which any external factor, for example, the centrifugal force or a magnetic field, acting on the given chromatographic system, determines the character of the movement of the mobile phase. Accordingly, centrifugal TLC, where the eluent moves mainly under the influence of centrifugal forces, has been assigned by the present authors to TLC methods with forced flow of the mobile phase (TLC-FF), like TLC-P.

We may note that descending TLC,[36] in which the force of gravity increases the rate of movement of the mobile phase compared with the ascending and horizontal variants of elution, could also be included in TLC-FF. However, because of the week influence of the gravitational component on elution,[37] this method is regarded only as a variant of continuous TLC.

A classification of the methods of TLC-CF is presented below. It demonstrates the possibilities of different variants of TLC-CF as regards the control of the flow of the mobile phase. In the TLC-P method (group C) the range of flow rates generated is virtually the same as in HPLC. The use of group B methods shortens the time of analysis by a factor of 2–5 and that of group A methods by a factor of 1.5–3 compared with traditional TLC.

Scheme



It is noteworthy that this proposed subdivision of TLC-CF methods into two groups is fairly arbitrary. For example, continuous elution conditions are realised in both centrifugal TLC and in TLC-P.

Table 1. Principal variants of liquid chromatography.

Characteristic	Traditional TLC	TLC with a controlled flow of mobile phase	CLC
Type of sorption system used	open	open or closed	closed
Cause of movement of mobile phase in sorption layer	capillary forces	capillary forces or pressure drop across layer	pressure drop
Flow rate of mobile phase lengthwise along the layer	variable	constant (controlled)	constant (controlled)
Possibility of controlling the flow of mobile phase	does not exist	exists	exists
Method of detecting components	on sorbent layer (static)	static and dynamic	in stream of mobile phase (dynamic)
Detection sensitivity*	high	high	high
Reproducibility	moderate	high	high
Number of samples analysed simultaneously	large	large	limited (usually one)
Use of sorption layer	single**	single**	repeated
Consumption of sorbent in series of analyses	large	minimal	minimal

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*CLC has the following advantages over traditional TLC: 1) absence of sorbent in the detection zone and 2) long light path in the measuring cell.

**Certain types of chromatographic plates in TLC can be used repeatedly after regeneration.

The principal variants of liquid chromatography are compared in Table 1 in terms of the sorption system employed, the character of the forces responsible for the movement of the mobile phase, etc.

III. CONTINUOUS COMBINED (TWO-STAGE) TLC

The term "continuous chromatography" is used in TLC in two senses. Firstly, in order to designate the process involving the separation of the sample which is continuously supplied into the chromatographic system. In continuous separation the mobile phase, on the one hand, and the sample and the sorbent layer, on the other, move in different directions. This method was first proposed by Martin[38] in planar (paper) chromatography and was realised by Guiochon et al.[29] Secondly the term is used to designate the variant of TLC in which only the flow of the mobile phase is continuous and the volume of this phase is greater than that necessary to wet the sorbent throughout the length of the chromatographic plate. Here and henceforth we shall only use the second meaning of the term "continuous chromatography".

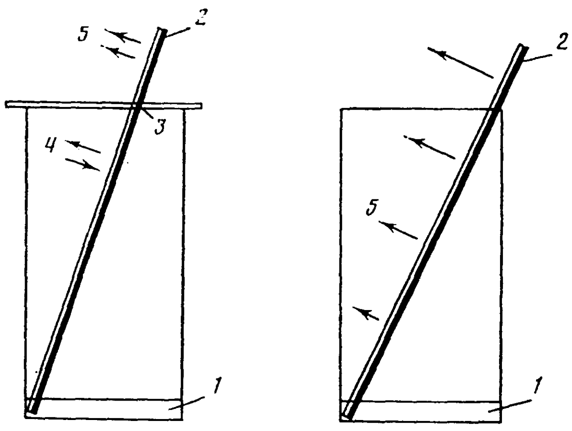
The principal aim of continuous TLC is the improvement of the separation of the mixture analysed by increaseing the distance over which the components to be separated migrate.

The initial variant of continuous TLC was the combined (two-stage) method. It was first used[40] in ascending chromatography on a free layer of alumina. The component to be separated was deposited on a dry layer of sorbent and elution was then carried out. The mobile phase was evaporated from one end of the chromatographic plate. In this case the separation process proceeds in exactly the same way as in the usual TLC after the attainment of the edge of the plate. The eluent reaches the edge of the plate, as stationary flow of the mobile phase is established along the sorbent layer. The flow rate is determined by the rate of migration of the front of the mobile phase at the end of the elution zone. Changes in the rate of movement of the solvent for the given combination of the mobile and stationary phases can be achieved by altering the length of the elution zone. [In a recently published study† an attempt was made to optimise the separation conditions in continuous TLC as a function of the rate constant of the movement of the eluent, the degree of separation, and the R_f for the components separated.]

Somewhat later Stanley and Vannier[41] and Mistryukov[42] developed novel and elegant methods for descending two-stage continuous TLC. Interesting procedures for the application of this variant of TLC have also been described in other communications.[43,44] However, the method involving constant flow of the mobile phase, proposed by Truter and Van Den Eijnden[45-47] and also the method of the gradient flow of the mobile phase or the evaporation method[48,49] are most frequently used. The differences between them are illustrated fairly clearly in Fig.1.

In order to carry out continuous TLC under identical conditions, Truter[45,47] suggested that a special lid be employed for the chromatographic chamber with a slit in which the plate is inserted. The mobile phase rapidly evaporates outside the limits of the chamber. Later a similar design was proposed independently by Van Den Eijnden[46] and was successfully applied in subsequent investigations.[50]

We may note certain useful modifications of Truter's method. In one investigation[51] a layer of charcoal was proposed to accelerate the process involving the "removal" of the mobile phase from the end of the chromatographic plate. The use of a paper wick for the removal of the eluent from the plate and for its supply through a slit to the outside of the chamber for the purpose of subsequent evaporation has been described.[52,53] The sorbent itself can be used to collect the mobile phase by placing a thick layer of the former ("roller") on the edge of the chromatographic plate.[54-56]



a *b*

Figure 1. Continuous TLC methods:[20] *a*) the method of the constant flow rate of the mobile phase;[45-47] *b*) the method of the flow rate gradient of the mobile phase along the layer:[48,49] 1) mobile phase; 2) thin-layer plate on which separation takes place; 3) slit in the lid of the chamber through which the upper end of the plate passes; 4) equilibrium in the sorption and desorption of the mobile phase vapour (the gas phase in the chamber is saturated by the mobile phase vapour); 5) evaporation of the mobile phase from the plate (a flow rate gradient of the mobile phase arises as a result of evaporation along the plate).

Thus a chamber saturated by the vapour of the mobile phase is used in Truter's method (Fig.1*a*) and its modifications and the solvent is evaporated outside its limits. For this reason, the rate of movement of the mobile phase along the plate is constant within the chamber.

Subsequently, chambers with a small volume of the gas phase came to be widely used. The first chamber of this type was proposed by Brenner and Niederwieser[57] specially for continuous TLC.[57] It was subsequently significantly improved by a number of investigators.[58-62] In our view, a novel chamber distinguished by simplicity and convenience in use, described by Soczewiński and co-workers,[61,62] merits special attention.

In the second known variant of continuous TLC (Fig.1*b*), the mobile phase is evaporated from the chromatographic plate already in the separation zone and during separation.[48,49] As a result of the partial evaporation of the eluent, the rate of movement of the mobile phase diminishes from the beginning to the end of the plate. This negative flow rate gradient results in a decrease of the width of the band (the band is compressed) and the separation is improved, which is especially important for the analysis of impurities. However, the main disadvantage of this interesting variant of continuous chromatography is inadequate reproducibility of the experimental conditions, which is naturally reflected also in the

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† E.K.Johnson, M.J.Wenning, R.E.J.Tecklenburg, and D.Nurok, J.High Resolution Chromatography and Chromatography Comm., 1986, 9, 285.

reproducibility of the retention parameters, the effectiveness, and the separation factors for the compound analysed.

Subsequently a new method, based on the intensification of the evaporation process—the so called "hot plate" method—was proposed and developed.[63,64] In this method a zone of increased temperature is created on the plate where accelerated evaporation results in an appreciable gradient of the flow rate of the mobile phase, leading to the compression of the chromatographic bands.

The variants of continuous TLC described (the evaporation and hot plate method) can be usefully employed, in our view, mainly for the concentration of impurities in analysis.

In the practical application of continuous chromatography, the isothermal variant is most often used.

All the variants examined presuppose a two-stage continuous TLC scheme. The presence of the first chromatographic stage and the deposition of the specimen to be separated on the dry sorbent greatly reduce the reproducibility and effectiveness of the continuous TLC method. Apart from this, the separation conditions selected with the aid of this method are fairly difficult to use in HPLC. This in fact stimulated the development of the single-stage continuous TLC method in which the sample is injected directly into the flow of mobile phase.[65] An important feature of this method is the detection of the components to be separated in the course of elution as in HPLC. For this reason, the single-stage continuous TLC will be considered in greater detail below in the Section devoted to the single-stage TLC with flow detection.

The continuous TLC method with sample injection into the stream of eluent is frequently referred to as flow TLC,[66] and the two-stage variant as continuous TLC. The concepts of "two- and single-stage continuous TLC" introduced in this review reflect the significant differences between these variants of TLC. This is necessary also because in the literature the flow variant is frequently referred to as continuous and conversely, although, as shown above, they differ fundamentally.

IV. CONTINUOUS SINGLE-STAGE TLC WITH FLOW DETECTION

An important independent stage in any chromatographic method is the assessment of the results of separation or the detection stage. In continuous TLC the following procedures can be used to determine the qualitative and quantitative compositions of the mixture analysed: (1) scanning (optical) of the plate with the separated chromatographic bands (see, for example, Refs.23 and 24), (2) continuous measurement of the concentrations of the compounds analysed in the moving eluent on the chromatographic plate or beyond it, and (3) a combination of both procedures: a method of detection in the flow of mobile phase for "light" components and a scanning method for "heavy" components or in general for components which are not eluted under the given conditions.

The first and third procedures appear to us more laborious compared with the second but they are optimal in the solution of many analytical problems. At the present time scanning is the commonest method for the automatic assessment of the results of separation in TLC.

The application of the second method actually implies the creation of a liquid-type thin-layer flow chromatograph. The role of the column in the latter is fulfilled by the thin-layer plate whose absorption layer is open from at least one side. Since in our view unjustifiably little attention has been devoted in the literature to the second variant of continuous TLC, although it makes it possible to reduce significantly the amount of labour involved in TLC whilst retaining its traditional advantages, it appears useful to discuss this method in greater detail. Previously it was considered only in a monograph[67] and in a review.[68]

The consideration of the method of continuous TLC with flow detection in a review devoted to different ways of controlling the mobile phase can be justified by the fact that the single-stage continuous (flow) TLC method was first devised precisely as a variant of continuous TLC with flow detection. The application of a flow detector assisted in a more successful development of continuous TLC.

The method of continuous TLC was initially developed for the rapid selection of experimental conditions in column liquid chromatography.[65]

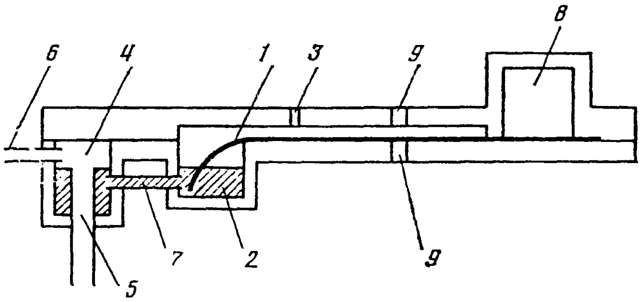

Figure 2. Schematic illustration of the first thin-layer chromatograph:[65] 1) TLC plate on a flexible transparent support; 2) reservoir for the mobile liquid phase; 3) aperture in the cover plate for the introduction of the sample onto the chromatographic plate; 4) preliminary chamber for the mobile phase with the drain tube *5*; 6) tube for the supply of the mobile phase; 7) connecting tube; 8) reduced pressure chamber for the evaporation of the mobile phase; 9) apertures for detection.

The thin-layer chromatograph employed by Schmid et al.[65] is shown in Fig.2. The constancy of the supply of the mobile phase is ensured by maintaining a virtually constant level of liquid in the working reservoir *2*, which communicates with the chamber *4*. The sample is injected from a micropipette via the aperture *3* in the upper lid. We may note that, in order to compensate for the possible errors in the measurement, a double chromatographic system is used. The two parts of a single flexible thin-layer plate work independently: in the chromatograph there are two apertures in the upper lid for the injection of the samples analysed and two apertures for the light guides with the aid of which the results of separation are recorded. The light guides, connected to a light source, are fitted with a green filter (550 nm). A photoresistor is used as the radiation detector. The liquid mobile phase is removed from the plate in chamber *8* under vacuum. The distance between the site of sample injection and the detection region is about 4 cm.

Fig.3 presents as an example the chromatogram of a mixture of dyes obtained on a thin-layer chromatograph of the first type. The parameters of the chromatographic bands of the dyes separated are listed in Table 2.[65] Taking into account the fact that the data presented in Table 2 refer to a short length of the layer (4 cm), they must be regarded as entirely satisfactory. For comparison, we may note that the columns used in the initial period of the development of gas–liquid chromatography were characterised by an efficiency close to that given in Table 2.

The method of continuous TLC with flow detection has been subjected to a general assessment.[69] It was shown that the continous-eluent planar chromatography can be used to separate both organic and inorganic compounds and that not only inorganic but also organic adsorbents, including ion-exchange adsorbents, can be employed as the stationary planar phase. In many instances it is useful to employ chromatographic paper as the sorbent in planar chromatography. Different gradient methods for the improvement of separation and, in particular, methods based on the use of sorption layers of different shape are of interest.[70,71]

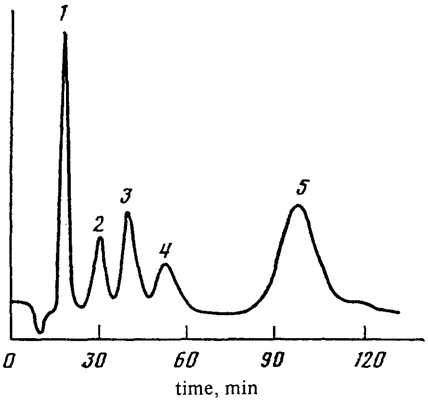

Figure 3. Chromatogram of a mixture of azo-dyes obtained on the first thin-layer chromatograph;[65] separation conditions: stationary phase—"Polygram Sil C" TLC plate, thickness of silica gel layer 0.25 mm, mobile phase—toluene mixed with 2% of ethanol; the designation of the peaks correspond to the numbers of the dyes in Table 2.

Table 2. Characteristics of the separation of azo-dyes under the conditions of continuous TLC with flow detection (mobile phase—toluene).[65]

Dye	t, min	c, mm	N, t.p.
N-Ethyl-1-[(*p*-phenylazophenyl)azo]-2-naphthylamine	17.5	4.5	648
1-[(*p*-n-Butylphenyl)azo]-2-naphthol	39	10	654
1-[(*p*-Methoxyphenyl)azo]-2-naphthol	61	17	501
1-[(*m*-Methoxyphenyl)azo]-2-naphthol	90	25	506
1-[(*o*-Methoxyphenyl)azo]-2-naphthol	162	41	683

Notation: t is the retention time, c the width of the separated component band, and N the number of theoretical plates (t.p.).

Continuous planar chromatography with flow detection makes it possible to employ the advantages of two main methods of liquid chromatography: the planar method characterised by flexibility and ease of replacement of the column-plate, economy, etc. and the column method which ensures, a high reproducibility of the retention parameters, a high degree of automation of the process, etc.

The method of continuous-eluent chromatography with flow detection can be applied in two versions: version I—the specimen analysed is deposited on the dry sorption layer and elution is then carried out by means of a flow of the mobile phase (the traditional method of sample deposition in TLC) and the components separated are detected by means of a flow detector; version II—the specimen analysed is deposited on the sorption layer wetted by the moving mobile phase and the components separated are detected by the flow detector (the method used in continuous TLC[61]).

In order to assess these versions of sample injection in continuous TLC, two series of measurements, comprising seven repeated separations on the same plate, were carried out.[69] The average rates of movement of azo-dyes on the TLC plate obtained using both versions as well as the reproducibility of these quantities are presented in Table 3.[69] The maximum deviation of the rate of movement of the chromatographic band from its average value (ψ_{max}, %) was used as the characteristic of the reproducibility. The measurements were performed using two mobile phases: benzene and toluene. Table 3 shows that the linear rate of migration of the chromatographic band (or the retention parameter) is reproducible, under conditions where the sample is injected into the stream of eluent (version II), with a random error 6–10 times smaller than in the deposition of the sample on the dry sorbent layer (version I). The time of analysis, determined from the retention time of the last extra component, was the same for both versions, but the retention times of light components are shorter for version I, apparently because of the higher flow rate in the initial period of the spreading of the mobile phase through the dry sorbent and the presence of a region of unsaturation near the solvent front.

Table 3. The average rates of migration of azo-dyes U_a on the chromatographic plate and the characteristic of their reproducibility $\psi_{max} = (\Delta U_{max}/\bar{U}_a) \times 100\%$ under the conditions of continuous TLC with the substance analysed introduced onto the dry layer of sorbent (variant I) and on the sorption layer wetted by the moving eluent (variant II).[69]

Sorbent (stationary phase)	Azo-dye	$\bar{U}_a$, mm min^{-1}				ψ_{max}, %	
		benzene (I)	toluene (I)	benzene (II)	toluene (II)	benzene (I)	toluene (I)
KSK silica gel + 5% of gypsum	*1*	1.82	1.70	1.27	0.99	22	2
	2	0.95	0.37	0.69	0,66	20	0
	3	0.57	0.46	0,54	0.38	7	2
	4	0,42	0.32	0,41	0,28	12	2
	5	0.30	0.21	0.30	0,20	10	0
Kieselgel 60F 254	*1*	2.40	2,18	2,00	0.92	16	1
	2	1.72	0.71	1,33	0,42	21	1
	3	0.90	0.33	0,67	0,24	13	0
	4	0.50	0.22	0,45	0.18	8	2
	5	0.30	0.10	0.31	0.11	4	2
Silpearl + 5% of gypsum	*1*	3.87	2.50	2.29	2.00	13	1
	2	1.56	0.92	1,21	0.88	16	1
	3	1.04	0,58	0.89	0,51	11	0
	4	0.65	0.33	0,60	0.30	8	2
	5	0.48	0,22	0,48	0,22	6	0

Notation: ΔU_{max} is the maximum deviation from the average rate of migration of the azo-dye in a series of experiments; 1) azobenzene; 2) Dimethyl Yellow; 3) *p*-methoxyazobenzene; 4) *p*-aminoazobenzene; 5) Sudan-III.

Analogous results have been obtained in the separation of aminoacids. Chromatograms of mixtures of dyes and aminoacids are presented in Fig. 4. The variation of the base line in the region of light (weakly retained) components on chromatograms *a* and *c* can be accounted for by the fact that, when the sample analysed is deposited on the dry sorbent, the arrival at the detector of the front of the mobile phase is accompoanied by a gradual alteration of the signal as a result of the movement through the detector of the unsaturation zone with a variable content of the eluent. When the sample is deposited on the sorbent layer and the stream of eluent is moving at a constant rate, this phenomenon is naturally not observed (chromatograms *b* and *d*).

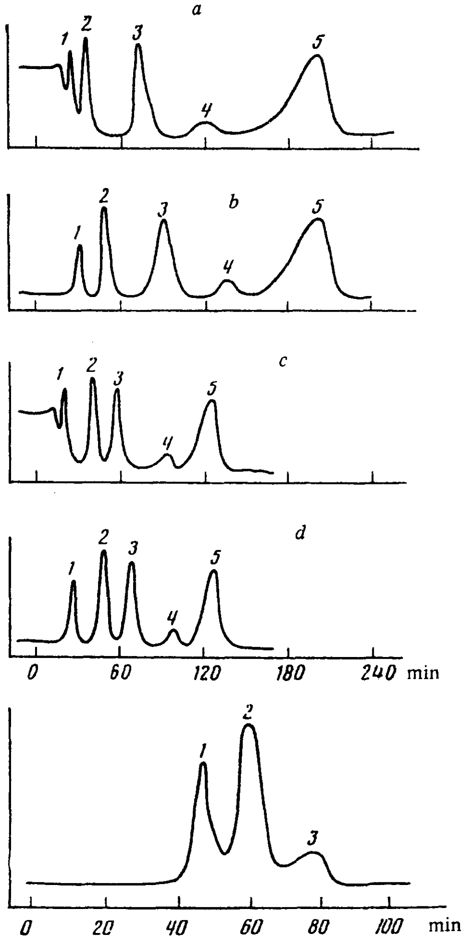

Figure 4. Chromatograms of mixtures of azo-dyes and amino-acids obtained on a thin-layer chromatograph:[69] *a*)–*d*) separation of a mixture of five azo-dyes (the designations are indicated in Table 3) on plates with "Kieselgel 60F 254" silica gel from the Merck Company (*a* and *b*) and "Silpearl" silica gel from the Cavalier Company (*c* and *d*); mobile phase—benzene, 600 nl sample introduced onto the dry layer of sorbent (*a* and *c*) or onto a layer of sorbent with a moving stream of eluent (*b* and *d*); *e*) separation of a mixture of 4-aminosalicylic acid (1), tryptophan (2), and histidine (3); stationary phase—"Silpearl" silica gel + 5% of gypsum, mobile phase—70 : 30 ethanol–water mixture; sample introduced onto the layer of sorbent with a flowing eluent; distance from the point of sample injection to detection zone 40 mm.

Since in the case where the sample is injected on the sorbent layer with the eluent in continuous TLC with flow detection (CTLC-FD) the separation process does not differ in essence from those occurring in column chromatography, this version of TLC is apparently one of the most rational procedures for the selection of optimum separation conditions in liquid column chromatography, to which attention was drawn by Schmid and Cramer.[65] The possibilities of CTLC-FD as regards the optimisation of separation conditions have been demonstrated in relation to the analysis of a mixture of dyes.[72] However, in our view, this method is undoubtedly also of independent importance. For this reason, we may note some of its positive features. Firstly, CTLC-FD makes it possible to replace the mobile and stationary phases easily and simply. Secondly, the method permits the analysis of specimens containing components which are not in fact eluted, since the periodic replacement of the thin-layer plate presents no difficulties. Thirdly, the method approaches column chromatography as regards the level of automation.

It is important to note that the injection of the sample into the stream of mobile phase beyond the line of the solvent front makes it possible to obtain more symmetrical peaks.[62] Thus this method of sample injection is of interest also for the usual variants of TLC. CTLC-FD occupies an intermediate position between the two- and single-stage variants of continuous TLC, since the eluent flow has not yet reached a steady state despite the specimen being injected into it.

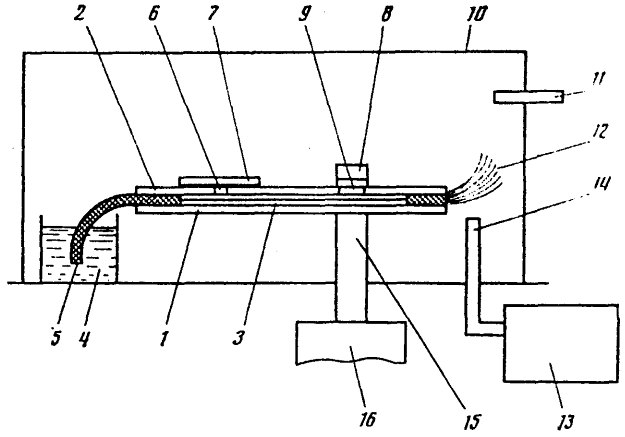

Figure 5. Schematic illustration of a thin-layer chromatograph:[69] 1) base (lower lid) of the chamber for the thin-layer plate; 2) upper lid of the chamber; 3) plate with sorption layer; 4) compartment for the mobile phase; 5) paper wick; 6) window for the introduction of the sample to be analysed; 7) lid; 8) radioluminescent light source; 9) slit diaphragm; 10) opaque jacket; 11) tube for the removal of air with the mobile phase vapour; 12) wick for the evaporation of the mobile phase; 13) air microcompressor; 14) pipeline for the supply of air; 15) light guide; 16) photoelectric multiplier.

The design of the apparatus is important in any experimental method. A thin-layer chromatograph, differing somewhat from the first instrument,[65] has been described by Berezkin et al.[69] This liquid-type chromatograph is illustrated schematically in Fig.5. A wick exposed to a strem of air and not an evacuated chamber, as in the study of Schmid et al.,[65] is used here to remove the solvent from the chromatographic plate. The employment of the wick for the supply of solvent to the plate permitted a greater variety of types of plates which can be used in the thin-layer chromatograph. In particular, in this instrument one can employ plates on a solid support. The use of a radioluminescent light source[73] permitted a simplification of the design and the employment of sources with different maxima in their emission spectra permitted the expansion of the region of applicability of the spectral detector. Not only glass but quartz plates are used as the material of the support for the adsorption layer, which creates the possibility of measurements in the ultraviolet part of the spectrum.[69] Other solutions have also been described.[74] They are based on the use of a small aperture in the sorption layer on the plate, which is usually opaque, as the optical microcuvette of the detector, where the concentrations of the compounds separated in the stream of mobile phase are measured. The filling of this aperture by the mobile phase does not entail an appreciable distortion of the chromatographic bands of the components separated. Fig.6 illustrates the possible types of microcuvettes in a thin-layer chromatographic plate.[74] The application of microcuvettes increases the sensitivity of the determination by a factor of 1.5–10 compared with variants in which there is a thin layer of sorbent in the path of the measured emission.[75] The diameter of the microcuvette does not exceed 1–3 mm. The possibility of using microcuvettes for the electrochemical detection of compounds separated has also been noted.[75]

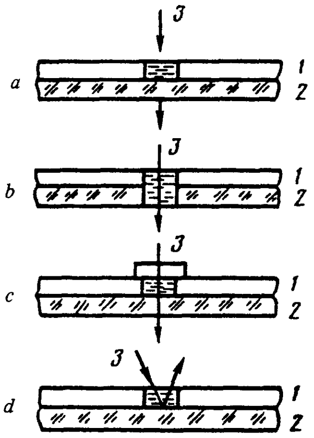

Figure 6. Types of optical flow microcuvettes in the TLC plate:[74] *a*) microcuvette in the sorption layer; *b*) microcuvette in the sorption layer and the support; *c*) closed microcuvette in the sorption layer; *d*) microcuvette in the sorption layer deposited on a support with a reflecting surface; 1) sorption layer; 2) support; 3) direction of light flux.

The efficiency of the separation when plates prepared in the laboratory with a thickness of the layer of 0.4 mm and a working length of the layer of 100 mm are used was $N = 700$ theoretical plates for the Sudan dye. The use of a plate from the Merck Company for high performance TLC made it possible to increase the efficiency to 3450 theoretical plates (for a working length of the layer of 60 mm).[69] This is significantly greater than the value obtained by Schmid et al.[65]

An interesting and promising trend in the development of flow TLC is its use for the separation of various compounds on various mobile phases consisting of two and more components. In chromatography under the conditions of single-stage continuous TLC, the "separation into layers" of the components of the mobile phase is unlikely, in contrast to traditional TLC.[21] This makes it possible to employ complex mobile phases for the separation of various sytems[72,76,77] and also to carry out the separation under the conditions of gradient elution.[78] The method and theory of continuous TLC separation using multicomponent mobile phases have been described in a recent study#. In the same investigation it was also shown that the data on separation obtained by continuous TLC agree satisfactorily with the results of separation by the HPLC method and can therefore be usefully employed for the optimisation of the separation conditions in HPLC.

The CTLC-FD method can be used successfully to estimate the separating properties of solvent powders,[79] which leads to yet another possibility, in principle, of employing TLC for physicochemical measurements.

We believe that, in analysing the prospects for the development of continuous TLC with flow detection, one should turn ones attention to the possibility of using slightly modified standard equipment for CTLC-FD, for example, a chromatograph with a U-chamber[80] as well as detectors based on the employment of laser-excited fluorescence,[81] photoionisation,[82] photoacoustic spectroscopy,[83] etc.

V. CONTINUOUS TLC WITH A MOVING ATTACHED LAYER OF SORBENT

A way[29,32,84] of increasing the efficiency of the separation per unit time is to increase the rate of elution and the distance over which the separation takes place. High flow rates of the mobile phase and high rates of continuous TLC can be achieved by shortening the elution zone,[37] which decreases in its turn the total number of effective theoretical plates. Separation in continuous TLC using a long elution zone entails a considerable fall in the flow rate of the eluent and hence a significant decrease of the specific efficiency.

Saunders and Snyder[85] have proposed an interesting solution of the problem of increasing the specific and general efficiency by increasing the rate of elution with a simultaneous increase of the distance over which the components separated migrate in the course of analysis under the conditions of continuous TLC. They developed a method in which an infinite strip on which the sorbent has been deposited moves in the direction opposite to that of the movement of the eluting substances. This method has been called drum TLC.[85] It is based on the fact that in the course of elution the distance between the front of the mobile phase and the site where it is supplied remains unchanged. By maintaining this distance as small as possible, one achieves high rates of elution. The separation in drum TLC takes place in the following manner. The plate on a flexible base is attached to a cylinder, the specimen to be separated is deposited, and then the cylinder is lowered into the eluent in such a way that the specimen remains above the surface of the liquid eluent. After the front of the mobile phase has reached the evaporation line, the drum is made to rotate against the direction of the migration of the eluent at a rate equal to that of the frontal migration but having the opposite sign. Thus the separating layer migrates relative to the spot and the immersion and

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#E.Soczewiński, in "Planar Chromatography", Vol.1 (Edited by R.E.Kaiser), Huethig, Heidelberg, 1986, p.79.

evaporation (of the front) lines at the same rate. Consequently the components separated can be eluted through a sorption layer of any length at a fairly high rate. The authors[85] showed that the method of drum TLC is a more effective and shorter analytical procedure than the traditional and usual continuous TLC and its efficiency is also superior to that of centrifugal TLC.

However, drum TLC, which gives rise to highly effective and rapid separation, suffers from a series of limitations. Firstly, this method makes it possible to separate only substances which differ only slightly in their R_f. Secondly, it is fairly difficult to maintain the necessary rate of rotation of the drum in the separation of colourless substances. Nevertheless, this method, which is relatively unsuitable for the separation of multicomponent mixtures consisting of substances with markedly different R_f, can prove to be extremely effective for the separation and analysis of substances having similar properties, for example, optical isomers.

A principle analogous to that employed in drum TLC has been used in the method of three-chamber TLC.[86] In this case the chromatography is achieved on a long looped foil strip coated by a thin layer of sorbent. During its movement, the foil enters the elution device consisting of three glass chambers (Fig.7).

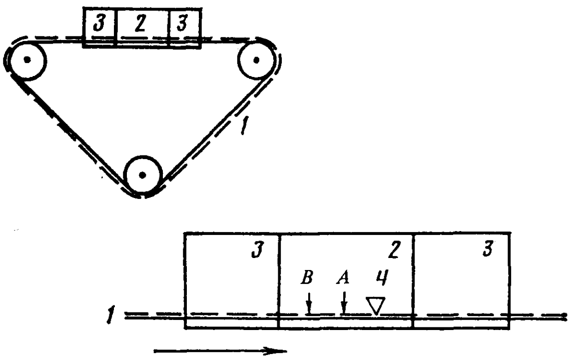

Figure 7. Schematic illustration of three-chamber TLC:[86] 1) foil with chromatographic layer; 2) main chamber; 3) lateral chambers; 4) channel for the supply of the solvent; A) and B) substances to be separated.

The separation takes place in the middle chamber. The other two serve for the evaporation of the solvent from the layer of sorbent. The rate of movement of the foil with the adsorbent is regulated by means of an electric motor connected to rollers. The mixture separated is deposited on the sorbent and placed in the middle chamber through which eluent is then supplied. During chromatography, the rate of movement of the strip should be such that the component to be determined is at the same distance from the eluent front throughout. At the end of the chromatographic process, the speed of the chromatogram is increased and all the components separated are moved in succession to the side opposite to that where the eluent is supplied. After drying each chromatographic band, a clear cut separation of the specimen over a comparatively short distance is achieved.

A method similar to drum TLC has been described by Halpaap and Bausch.[87] In this method the film with the sorbent layer is rewound from one coil to another coil underneath. As in drum TLC, the latter is immersed in the reservoir with the eluent. In this case the separation section is much longer than the circumference of the cylinder in drum TLC. The authors[87] carried out the separation process on sections of the sorption layer of different lengths.

It is noteworthy that the continuous TLC methods considered here are variants of eluent chromatography with the layer of sorbent moving relative to the point of supply of the eluent.[88,89]

VI. CENTRIFUGAL TLC

Centrifugal chromatography, first proposed[90] as a variant of paper chromatography, was subsequently used in TLC.[91,92] This method is applied in two versions: the linear and radial versions.[85] In the radial or circular version of the centrifugal TLC, the system chromatographed rotates about its axis so that the movement of the mobile phase is accelerated by centrifugal forces, as in the linear version. In the radial centrifugal TLC, the mobile phase is supplied to the centre of a circular sorption system. The flow rate of the mobile phase can be regulated by means of a micropump. According to the authors,[85] centrifugal forces play the same role as pressure in HPLC.

In linear centrifugal TLC, the quantity equivalent to pressure in HPLC can be expressed by the relation[85]

$$P = \rho\omega^2 Z_f^2/2 , \qquad (2)$$

where ρ is the density of the mobile phase, ω the angular velocity of the plate, and Z_f the distance from the point of supply to the front of the mobile phase.

On the basis of the foregoing, centrifugal TLC can be classified as a TLC method with a controlled forced flow. The flow is stabilised by employing continuous TLC conditions and the rate of elution is regulated by the rate of rotation of the support. We may note that the rate of elution is directly proportional to the square of the angular velocity.[85]

A detailed critical review on centrifugal chromatography,[93] written in 1964, has not lost its importance today. The authors[4] believe that the economy of time in the elution of thin-layer chromatograms by centrifugal TLC is not very great. It is impossible to agree fully with this view. For very long separations, this method is undoubtedly economically justified and it has continued to be used in analytical practice in recent years: the reversed phase centrifugal TLC has been used successfully for the separation of polar compounds of plant origin § and the ion-exchange version of centrifugal TLC has been employed for the determination of Fe, Co, Ni, Cu, Hg, and other metals ¶. Different aspects of the application of centrifugal TLC have been discussed in a number of studies.[94–96] The possibilities of centrifugal TLC for preparative separation have been demonstrated by Stahl and Müller,[97] who showed that the specific sample charge in this method can amount to between 10 and 1000 mg per millimetre of the thickness of the absorption layer for one compound. The results of a detailed study[97] are of interest not only for preparative but also for analytical chromatography. Fig.8 [97] illustrates the dependence of the separation time on the overall flow rate of the mobile phase. It follows from the data presented that an increase in the flow rate of the mobile phase leads to a significant shortening of the chromatographic process, which is particularly pronounced in the region of low rates. Fig.9 [97] presents the dependence of the separation

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§ F.Orsini and L.Verotta, J.Chromatog., 1985, **349**, 69.

¶ Song Yirong and Yin Bohai, Xibei Daxue Xuebao, Ziran Kexueban, 1985, **15**(2), 56; Chem.Abs., 1986, **104**, 179, 193.

factors for hydrazones (dyes) on the volume rate of supply of the mobile phase and the rate of rotation of the chromatographic system. The maximum resolution for the average flow rate of the mobile phase (5.2–3.5 ml min^{-1}) was obtained in the region of relatively low rates of rotation of the chromatographic system (~750 rev min^{-1}).

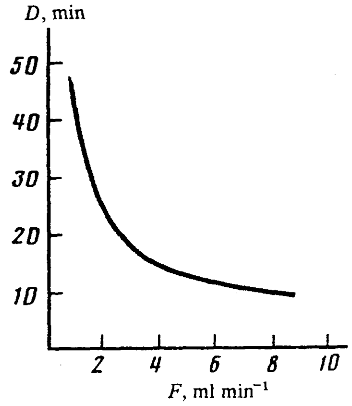

Figure 8. Dependence of the separation time D on the volume flow rate of the mobile phase F; experimental conditions: stationary phase—silica gel 60 with 1.5% of acronal, mobile phase—80:20 hexane–ethyl acetate mixture, rate of rotation 750 rev min^{-1}.[97]

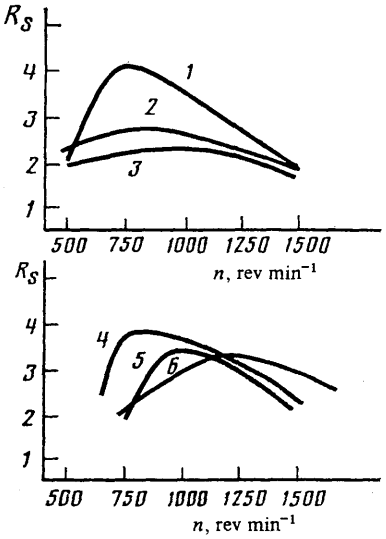

Figure 9. Dependence of the separation factor R_S for hydrazone dyes on the rate of rotation of the chromatographic system n;[97] experimental conditions: stationary phase—silica gel 60 with 1.5% of acronal, mobile phase—80:20 hexane–ethyl acetate mixture, volume rate of supply of mobile phase to the chromatographic system (ml min^{-1}): 1) 3.5; 2) 2.1; 3) 1.1; 4) 5.2; 5) 7.1; 6) 8.8.

In comparing preparative centrifugal TLC with traditional preparative TLC and column chromatography, the authors[97] arrived at the justified conclusion that this method has definite advantages.

Attention should be drawn to the recent appearance of several new methods and variants of apparatus involving centrifugal TLC.[98–100] A new method of planar preparative chromatography—sequential centrifugal layer chromatography (SCLS)—has been described.[98] According to the authors of the method, it combines the advantages of preparative and analytical centrifugal, antiradial, and sequential TLC. The apparatus for SCLC makes it possible to carry out circular chromatography with centrifugation at different rates of rotation. The supply of the eluent to any point on the plate makes it possible to separate additionally the individual components using individual mobile phases. Furthermore, there is a possibility of carrying out antiradial chromatography under the influence of capillary forces. Thus the SCLC method is in fact a hybrid procedure which expands the possibilities of centrifugal TLC.

A new centrifugal countercurrent chromatograph for partition chromatography has been proposed by Japanese investigators.[99] A rapid preparative separation of a series of mixtures of aminoacids, sugars, and saturated aliphatic acids has been achieved with its aid.

The possibilities of centrifugal TLC for a significant increase of the flow rate of the mobile phase in HPTLC have been demonstrated.[101] It has been shown that the results obtained in three-minute separation with centrifugation are equivalent to 12-minute separation with the aid of the usual circular TLC.

The method of centrifugal paper chromatography, its possibilities, and the prospects for its development have been considered in a review.[102]

The possibility of obtaining high flow rates of the mobile phase in centrifugal chromatography are limited. It is believed[85] that the use of rates of rotation at which pressures above 1 atm are created [see Eqn.(2)] would cause the rupture of the column of solvent and the mixing of air with the solvent at the point of its introduction. Yet another limitation is associated with the application of an open layer of sorbent in centrifugal chromatography: the increase in the resistance of the layer of sorbent with increase in the rate of elution can lead to the "spilling" of the eluent through the sorbent. This is in fact why centrifugal chromatography does not permit the attainment of the same high flow rates of the mobile phase as in HPLC.

VII. THIN-LAYER CHROMATOGRAPHY UNDER PRESSURE

The simplest, effective, and traditional method of attaining a high flow rate of the mobile phase or the layer of sorbent involves the creation of an excess pressure at the start of the sorption layer. However, an enclosed layer must be used to apply this method. This solution was proposed for TLC in 1977 by Hungarian investigators.[35] In fact, this is a variant of thin-layer column liquid chromatography, because the column contains a thin layer of sorbent. Thin-layer plates with an enclosed layer were known earlier in planar chromatography (see, for example, Refs.103–105), but they were not used in liquid chromatography.

A schematic illustration of a simple and novel apparatus[35,106,107] for TLC under pressure is presented in Fig.10. It is especially noteworthy that standard plates of any type can be used in this apparatus. The support of the chromatographic plate serves as the lower wall of the planar column, while the upper wall consists of the polymeric film-membrane *8*, which is clamped to the adsorption layer *6* of the plate *7* under the pressure of gas or liquid. The pressure at the inlet to a planar chromatographic column should naturally be lower than the external pressure used to clamp the polymer film to the adsorption layer in order to form a closed chromatographic system—"column". Owing to edge effects, which significantly disturb the front of the mobile phase and disorganise the solvent stream under the conditions of increased pressure, in applying the linear TLC-P method it is essential to use either special plates with the sorption layer on a silica gel, alumina, or talc base[108] alternatively a material inert towards the given mobile phase must be deposited on the edges of standard plates. Paraffin or various plastics are used as materials of this kind. Fig.11 illustrates plates for TLC-P. In order to form the linear front of the mobile phase over the adsorption layer of the TLC plate, an insert with a channel connected to the aperture through which the solvent is supplied to the planar chromatographic system is introduced. The channel can be made also directly in the adsorption layer having removed part of the sorbent.[109] Under the conditions of increased pressure, the solvent very rapidly fills the capillary channel, which thus becomes a linear source of the solvent and actually fulfills in TLC-P the role of a small bath with a mobile phase used in the usual TLC. Fig.11 illustrates two versions of linear TLC on standard plates: *a*—elution in one direction and *b*—elution in two opposite directions. Two dimensional separation,[110] which is known to be characterised by the maximum peak capacity compared with other TLC methods, can be achieved by means of TLC-P.

Other variants of traditional TLC, differing in the form of the sorption layer, can also be used successfully in the TLC-P method: the triangular,[71] anti-circular,[111] and circular[23] variants. The use of circular chromatography in this variant of TLC has been described, for example, in Refs.107, 109, and 112. It is apparently simplest to apply this variant of TLC-P in practice, since there is virtually no need to cover the edge of the plate by any material. The samples analysed are usually deposited on the plate in a preliminary step before the plate is placed in the TLC-P apparatus. A number of studies[113–116] have been devoted to questions of the optimisation of the operating conditions in TLC-P. Kalász and Nagy[116] believe that the optimum linear flow rate of the mobile phase depends on the size of the particles of the sorption layer and is in the range 0.10–0.28 mm s^{-1}. The TLC-P method was subsequently developed in other investigations.[117–120]

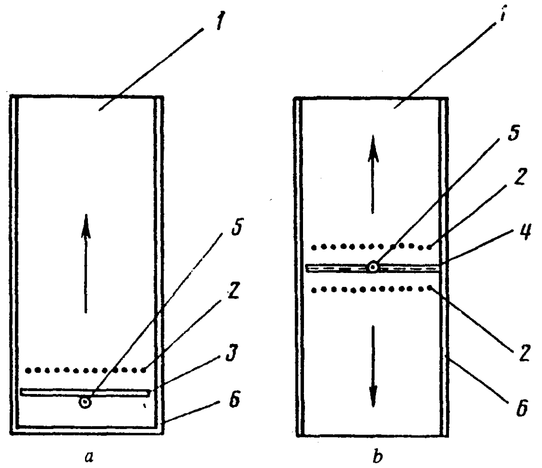

Figure 11. Linear elution in one direction (*a*) and in two opposite directions (*b*) in TLC-P:[109] 1) chromatographic plate; 2) region of deposition of samples analysed on the sorbent layer; 3) capillary channel in the adsorption layer for the organisation of the linear mobile phase front; 4) insert with a capillary channel for the mobile phase; 5) inlet for eluent; 6) edge impregnated with inert material.

The characteristics of the movement of the mobile phase front in TLC-P differ from those familiar in traditional TLC, for which a quadratic law holds[9,22–25] [see Eqn.(1)], while in the vicinity of the front there is an unsaturation zone.[7,27] It has been established (see, for example, Lengyel et al.[109]) that the following equation is valid for linear TLC-P:

$$Z_f = k_{\mathrm{TLC\text{-}P}}t, \qquad (3)$$

where Z_f is the distance of the solvent front from the line at which the mobile phase is introduced, t the time, and $k_{\mathrm{TLC\text{-}P}}$ a constant. This relation holds under the following conditions: (1) the volume rate of supply of the mobile phase in

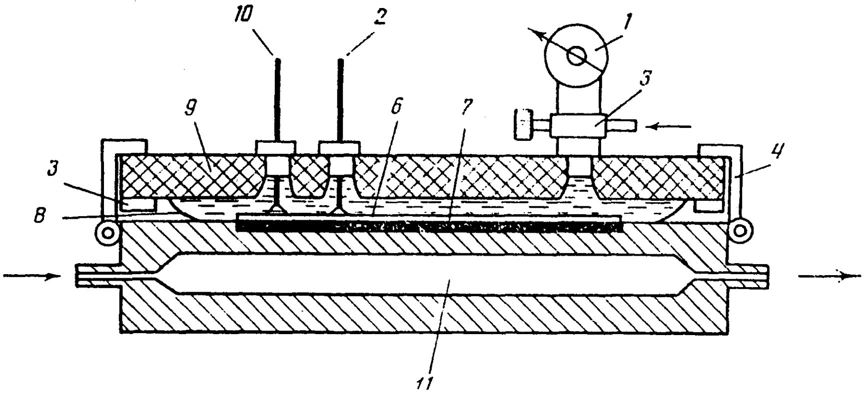

Figure 10. Schematic illustration of the apparatus for TLC under pressure:[106] 1) manometer; 2) device for the introduction of the specimen to be analysed under pressure; 3) inlet for gas or liquid; 4) clamps; 5) sealing washer; 6) sorbent layer; 7) glass or plastic support; 8) polymer membrane; 9) transparent lik; 10) device for the introduction of the mobile phase; 11) thermostatic device.

the chromatographic system F is constant and (2) the layer of sorbent is regularly packed so that its width is b, its thickness d, and the free volume fraction is β. The time t during which the mobile phase front migrates over a distance Z_f is defined by the relation

$$t=(Z_f b d\beta)/F\,,$$

whence

$$Z_f=(F/bd\beta)\,t\,. \tag{4}$$

It follows from Eqns.(3) and (4) that

$$U_f=k_{\mathrm{TCL\text{-}P}}=F/bd\beta,$$

where U_f is the linear rate of migration of the front.

Knowing the parameters b, d, and β of the sorption layer and also the volume rate of supply of the mobile phase to the system, it is possible to determine the linear rate of supply of the mobile phase.

On the basis of material balance equations, the following relations can be formulated for circular TLC-P:

$$t=\pi Z_{f\text{-}r}^2 d\beta/F\,,$$

where Z_{f-r} is the radius of the mobile phase front on the chromatogram and

$$Z_{f\text{-}r}=\left(\frac{Ft}{\pi d\beta}\right)^{1/2}, \tag{5}$$

$$U_{f\text{-}r}=\frac{dZ_{f\text{-}r}}{dt}=\frac{1}{2}\left(\frac{F}{\pi d\beta t}\right)^{1/2},$$

or

$$U_{f\text{-}r}=\frac{1}{2}\,\frac{F}{\pi d\beta Z_{f\text{-}r}}\,.$$

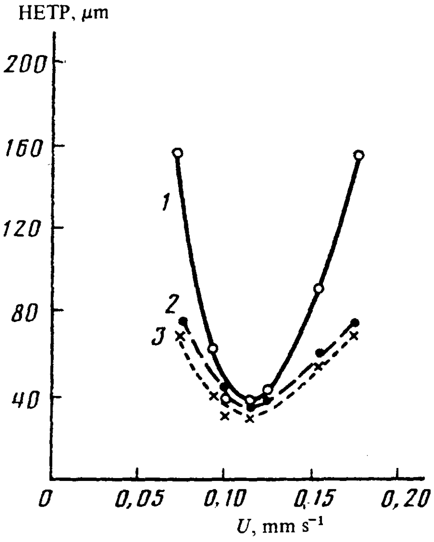

Figure 12. Dependence of the HETP on the linear flow rate of the mobile phase U;[131] stationary phase—200 × 200 mm plate (Fixion 50 × 8), mobile phase—sodium citrate buffer at pH 4.2; 1) arginine; 2) lysine; 3) histidine.

Thus the linear flow rate of the liquid mobile phase under the conditions of circular TLC-P is inversely proportional to Z_{f-r}. Consequently, under these conditions, the linear rate of migration of the eluent is not constant, decreasing as the point of the measurement moves away from the site at which the mobile phase is introduced. However, it is known that the efficiency of a chromatographic system, characterised by the height equivalent to the theoretical plate (HETP), depends significantly on the linear rate of migration of the mobile phase and this dependence has a sharp optimum. As an example, we may quote the dependence of the HETP on the linear flow rate of the mobile phase (see Fig.12). It follows from Fig.12 that the HETP depends fairly markedly on the linear rate of migration of the mobile phase. It therefore appears useful to carry out the chromatographic separation at a constant linear rate also in circular chromatography. This condition can be achieved by programming the flow rate of the eluent.

Since the flow rate of the mobile phase decreases as the front moves in the known variants of circular TLC-P, the HETP increases. As an example, Fig.13 presents data for the variation of the HETP as a function of the distance traversed by the mobile phase front. Evidently in linear TLC-P the efficiency hardly changes but it diminishes sharply when the elution methods traditional for TLC are used. It is noteworthy that the maximum efficiency is also attained in the case of linear TLC-P.

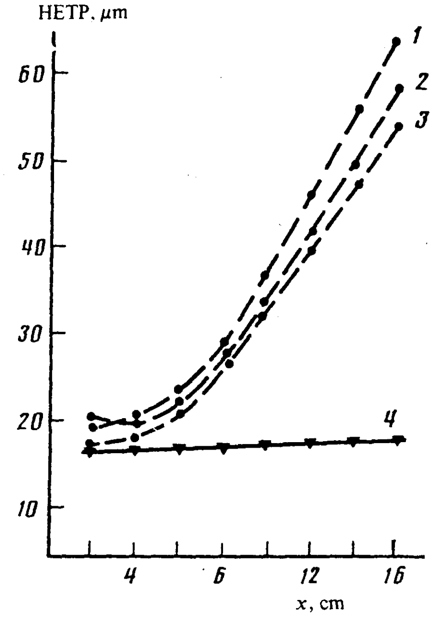

Figure 13. Dependence of the HETP on the distance traversed by the mobile phase front x [126] under the conditions of traditional TLC (curves 1–3) and TLC-P (curve 4): 1) unsaturated chamber; 2) ultramicrochamber; 3) saturated chamber; experimental conditions: stationary phase–silica gel 60 with 5 μm grain size, mobile phase—methylene chloride, sorbate—Butter Yellow dye.

Fig.14 presents two densitograms (chromatograms) for a mixture of compounds used as doping agents.[121] All the compounds are separated satisfactorily by the TLC-P method (Fig.14*a*) after 25 min; when traditional TLC is used (Fig. 14*b*), certain compounds cannot be separated at all (for example, compounds 2 and 3 and 5 and 6), while others are separated unsatisfactorily (for example, compounds 3 and 4 and 7 and 6), the separation time amounting to 95 min (almost four times more than in TLC-P).

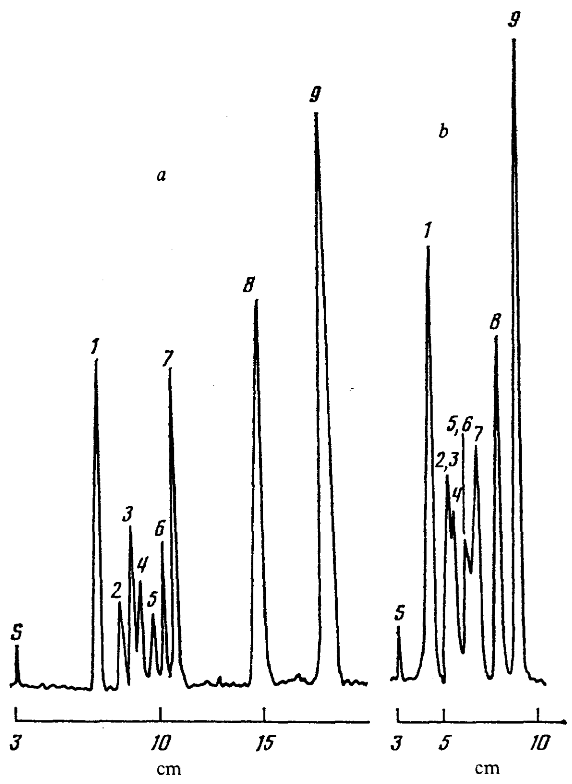

Figure 14. Separation of doping agents by TLC-P (*a*) and traditional TLC (*b*) methods:[121] 1) strychnine; 2) ephedrine; 3) methamphetamine; 4) phenmetrazine; 5) methylphenidate; 6) amphetamine; 7) desopimon; 8) coramin; 9) caffeine; S—start; stationary phase—silica gel 60 from the Merck Company, mobile phase—25 : 17 : 8 : 4 : 6 1-butanol—chloroform—ethyl ethyl ketone—water—acetic acid mixture; flow rate (for TLC- 0.85 cm min^{-1}.

Table 4. Some examples of the practical use of thin-layer chromatography under pressure.[108]

Compound analysed	Mobile phase
Essential oil	methylene chloride or benzene
Lipophilic dye	methylene chloride
Corticosteroids	nitromethane
Bile acids and their derivatives	ethyl acetate
Ergot alkaloids	acetonitrile
Dinitrophenylhydrazones of aliphatic aldehydes	diisopropyl ether
Essential oil	benzene–ethyl acetate (98 : 2)
Adducts of dimedone with aliphatic aldehydes	chloroform–ethyl acetate (95 : 5)
Aminoacids derived from nucleic acid bases, nucleosides	n-butyl alcohol–glacial acetic acid–water (4 : 1 : 1)
Poppy alkaloids	acetonitrile–water mixtures
Digitalis alkaloids	acetonitrile–water mixtures
Dinitrophenylhydrazones of aliphatic aldehydes	methanol–water and acetonitrile–water mixtures

The TLC-P method suffers from no limitations as regards the type of compounds to be analysed and is used to separate compounds of different classes: aminoacids and their derivatives,[122–124] the aflatoxins B_1, B_2, C_1, C_2, and M_1,[125] dyes,[126] and organic acids and their derivatives.[127] This method is used in reversed phase[128–130] and ion exchange TLC[131] and in phytochemistry.[132] Certain classes of compounds separated and the systems of mobile phases used for their separation are presented in Table 4. The possibilities of the TLC-P method have also been discussed in other studies.[133–142]

A variant of TLC-P different from that employed by Hungarian investigators[106,107] has been recently proposed by Kaiser and Rieder.[143] In this case the plate is positioned on a thermostatted base with the sorption layer downwards and is clamped to the latter with the successive deposition from above onto the support of the plate of a layer of silicon rubber and a thermostatted coating using a press developing a force up to 20 tonnes. The eluent is supplied from below onto the sorption layer at the centre of the plate or along its periphery. In the former case the circular version of TLC-P is achieved and in the second the antiradial version obtains. The eluent passes from a vessel, in which an excess pressure is established by supplying an inert gas at a high pressure. The main advantage of this variant of the device for TLC-P is the possibility of the relatively simple application of antiradial TLC-P.

The extensive experience gained in the development and study of the possibilities of the TLC-P method makes it possible to recommend it for a wide range of applications. At the present time Hungarian specialists have initiated the manufacture of commercial apparatus for TLC-P.[108,114,136,140]

In considering the prospects for the TLC-P method, we should like to draw attention to the usefulness of its variant with flow detection. When this method is employed for preparative separation, it is desirable to use one detector placed behind the sorption layer. We may note that we are unaware of studies in which the possibilities of the TLC-P method have been assessed as regards preparative separation, although this aspect of its practical application appears to be of great interest.

The variant of continuous TLC-P with a series of independent detectors, in which the chromatographic plate functions as a set of individual columns arranged in parallel, for the simultaneous and independent separation of a series of samples is promising for analytical separation.

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Analysis of Polycyclic Aromatic Hydrocarbons by High Performance Liquid Chromatography

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The review gives a systematic account of a survey of data on the high performance liquid chromatography of polycyclic aromatic hydrocarbons using phases of normal polarity and reversed phases. The factors influencing the parameters of the chromatographic separation of the above compounds are examined and the conditions for the analysis of polycyclic aromatic hydrocarbons in objects within the environment are presented.
The bibliography includes 318 references.

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I. INTRODUCTION

The monitoring of the content of polycyclic aromatic hydrocarbons (PAH) in various objects in the environment is very important. Since it has been demonstrated that the carcinogenic and mutagenic action of certain PAH depends on their composition and structure, the exact knowledge of the structure of each component of the complex mixture of PAH is essential for the determination of the total carcinogenic (mutagenic) potential of the test specimen.[1,2]

With increase of the intensity of man's action on nature during the XXth century, the entry of PAH into the environment has become more pronounced at an increasing rate. The principal anthropogenic sources of PAH are[3] internal combustion engines, boiler engines operating on solid and liquid fuels, metal casting, chemical, coke, and shale industries, self-igniting coal bearing rock, etc. Thus the exhaust gas from internal combustion engines contains more than 200 different components of which 160 are carcinogenic. In city air with intense automobile traffic and metallurgical and coke-chemical industries, the content of PAH can reach 1.5–2.5 μg/100 m^3 of air.[4] It has been suggested that the contribution of tobacco smoking to the overall level of the accumulation of PAH is small but has a very dangerous effect on human health.[5,6] More than 170 carcinogenic substances have been detected in tobacco smoke.[4] At the same time the accumulation of PAH in the Planet's biosphere is expressed by the impressive overall figure of 5000 tonnes annually;[7,8] PAH have been detected also in the air and atmospheric dust of industrially developed cities, in drinking water, in industrial waste water, in various marine organisms and deposits, in the work places of certain industries, in food products, etc.

The content of 3,4-benzopyrene, which is comparatively easy to determine, can serve as a fairly reliable criterion for the estimation of the overall content of PAH in objects in the environment.[2,7] Approximately 80% of 3,4-benzopyrene released can be transported over a distance in excess of 100 km and can influence the state of the environment in non-industrial regions.[8] During winter, the content of PAH in the atmosphere is usually several times greater than in the summer.[9]

Analysis of PAH is important for the hygienic assessment of the quality of the environment for the determination of the source of contamination by carcinogenic substances.[10] The possibility of direct analysis of PAH in various objects of the environment is determined primarily by the sensitivity of the method[11] and in many cases preliminary concentration of the sample is necessary. The most promising analytical methods for PAH are capillary and gas–liquid chromatography (GLC) and high performance liquid chromatography (HPLC).[5] The possibilities of capillary GLC become increasingly limited with increase of the molecular weight of the PAH and the method is unsuitable for the analysis of samples containing six and more aromatic nuclei in the molecule. Similar limitations apply to a much lesser extent to the analysis of PAH by the HPLC method and in recent years there has been an increase in the number of publications on the HPLC of various PAH.[5,10,12–24]

The present review covers the literature on the analysis of PAH by the HPLC method published between 1973 and 1983 inclusive and partly the literature in 1984–1985; the analytical methods using normal-polarity and reversed phases, gradient elution, and highly sensitive detection systems are examined. The review does not include studies on the separation of PAH using exclusion or ion-exchange chromatography.

II. SEPARATION BY NORMAL-PHASE CHROMATOGRAPHY

During many years, alumina and silica gel were the commonest sorbents for the separation of PAH. Microdisperse[25] or surface-porous silica gels[26] are most often used nowadays. Thin-layer chromatographic data obtains using saturated hydrocarbons as the mobile phases (MP) are as a rule employed for the selection of conditions in the preparation of PAH on packed columns. In the analysis of PAH with high molecular weights, the MP are modified by activating additives in order to intensify their eluting properties.[27–31]

In one of the first studies on the HPLC of PAH,[32] it was shown that a mixture of substances ranging from naphthalene to 1,2-benzopyrene is effectively separated on a 300 × 3 mm column filled with Spherosil XOA 400 (MP = iso-octane and cyclohexane). The sensitivity of the determination of the individual components with UV detection (at wavelengths of 250 and 220 nm) is approximately to within 2 ng.

The earlier attempts to correlate the chromatographic parameters with the structure of the PAH molecules are presented in a monograph.[21] It was noted that the content of unsubstituted PAH increases with increase of the molecular weight and of the number of carbon atoms in the molecule; with increase of the length of aliphatic side chains, the content of PA also increases as a rule.[33-37] The relation between the capacity factor of the test substance k', the adsorption energy S_a^0, and other parameters is:[21]

$$\lg k' = \lg V_a + \alpha (S_a^0 - A_s \varepsilon^0)\,, \tag{1}$$

where V_a is the volume of the adsorbent in the column, α the adsorption activity of the adsorbent, A_s the size of the adsorbate molecule, and ε_0 the eluting power of the mobile phase. When pentane is used as the MP, $\varepsilon^0 = 0$ and the expression simplifies:

$$\lg k' = \lg V_a + \alpha S_a^0\ . \tag{2}$$

The adsorption energy S^0 can be expressed by the equation[126]

$$S^0 = \sum_i Q_i^0 + \sum_i q_i^0\ , \tag{3}$$

where Q_i^0 are the additive contributions of the individual groups of the molecule to the overall adsorption energy and q_i^0 are the contributions determined taking into account the possibility of the interaction between the groups indicated. The retention parameters of alkylnaphthalenes and alkylphenanthrenes are described satisfactorily by Eqn.(2) only for compounds with unbranched groups; the presence of secondary alkyl groups induces a significant discrepancy between the experimental and calculated data.[33]

A systematic study of the chromatographic behaviour of alkylnaphthalenes and alkylphenanthrenes has been undertaken by Popl et al.,[33,38] who established that Snyder's empirical formula

$$S^0 = 0.31\, nC_a\ , \tag{4}$$

where C_a is the number of aromatic carbon atoms in the molecule, holds vigorously in the alumina–pentane system only for arenes whose molecules contain 1–3 aromatic nuclei; on passing to PAH with four nuclei and non-planar PAH, the deviations become considerable. The relation expressed by Eqn.(4) breaks down on passing from straight-chain groups to branched groups owing to steric hindrance to the adsorption of such compounds.

Acid–base interactions influence significantly the sorption process. The adsorption energies on sorbents of the type Al_2O_3 increase appreciably for PA with acidic hydrogen atoms (indene, fluorene, and benzofluorenes) and low ionisation potentials (anthracene, naphthacene, and pentacene).[38] The acidity of the Al_2O_3 surface influences significantly the retention sequence of the components and, when the standardisation of the sorbent is adequately reliable, this phenomenon can be used successfully for both group[39] and individual analyses.[40]

Alumina and silica gel differ significantly in their sorption characteristics owing to the different acidities and structures of their surfaces.[22,43-46] These differences are fairly clearly manifested in relation to the separation of the anthracene–fluoroanthene pair.[41,42] It is believed that the sorption of PAH on Al_2O_3 is determined by electrostatic interactions and that on SiO_2 by hydrogen bonds. Detailed investigation of the characteristics of the separation of PAH on different brands of silica gel has shown that the capacity coefficient depends on the difference between the changes in free energies,[47] partition coefficients, specific surfaces, packing densities of the sorbent, and the proportions of its particles of different size.[48,49] The alkyl groups in naphthalenes and phenanthrenes influence differently their sorption on Al_2O_3 and SiO_2.[33,50,51] It is noteworthy that certain cyclic aromatic compounds have retention parameters close to those of aromatic polymethyl-substituted hydrocarbons containing identical numbers of carbon atoms. This phenomenon has not so far been convincingly explained.

Isomers of PAH with substituents in different positions have significantly different Kovac indices.[38] For the same number of carbon atoms in a series of aromatic hydrocarbons, the retention indices either differ significantly, as, for example, in 1,4- and 2,3-dimethylnaphthalenes and 1- and 2-phenylnaphthalenes, or are approximately the same as in 1,7- and 1,3-dimethylnaphthalenes and 1- and 9-methylphenanthrenes. In the latter case liquid chromatography on reversed phases with a careful selection of the eluent can be usefully employed for separation.

Other sorbents are also used in the analysis of PAH. Thus isomeric benzopyrenes and coronene have been separated[52,53] on columns with cellulose acetate and polyamide. Cellulose[54] and macroporous polystyrene[55] are also employed to separate PAH. One must assume that mixed partition and adsorption processes occur for these and similar sorbents.[56] A significant disadvantage of these fillers is their low mechanical strength and it is therefore useful to deposit them on strong carriers. The deposition of picric acid,[57] melamine polymerisate,[58] Bentone,[34,59] and carbon black[60,315] on silica gel and the use of such deposits for the separation of aromatic hydrocarbons by the HPLC method have been described in a number of studies. A new packing material, namely porous carbon glass, has been proposed recently.[61] Using methylene chloride with the addition of 0.1% of 1,3-terphenyl as the MP, it has been possible to separate successfully into individual components a mixture consisting of five PAH. The modification of hexane by more polar solvents has been examined on Silasorb 600 silica gel.[301]

III. THE USE OF CHEMICALLY MODIFIED SORBENTS

One of the main criteria of the reliability of chromatographic determination is the reproducibility of the retention parameters. Classical adsorbents are modified even in the presence of a very small water content in the MP. The retention times of the components vary within wide limits because the chromatographic column is in a non-equilibrium state.[62] Difficulties therefore arise in the use of gradient elution, for example, in the analysis of high-molecular-weight PAH.[63]

The deficiencies of liquid–liquid partition chromatography are frequently more significant than its advantages. The stationary phases fixed on the carrier become unstable when MP with similar polarities are used; the instability is manifested to an even greater extent when a gradient MP with highly polar eluents is employed.[64] The separation of PAH exclusively on chemically bound stationary phases will be considered below because ~80% of all the separations by the HPLC method are carried out on such sorbents.[65]

1. Separation on Reversed Phases

In separation on reversed phases (RP) a non-polar adsorbent and a polar eluent are used. This system is universal for PAH, their reaction products, and their heterocyclic analogues. In this variant of liquid chromatography, the retention of the components is inversely proportional to their polarity and is determined both by the non-polar non-specific sorbate–sorbent interaction and by the polar specific sorbate–eluent interaction.[14] In the analysis of PAH on RP, the relations between such interactions are frequently fairly complex. With increase of the chain length of the MP, the capacity factors rapidly fall (Fig.1) which significantly complicates the analysis of multicomponent PAH mixtures.[66]

As a consequence of the unique properties and the wide availability of octadecylsilane (ODS) reversed phases, the majority of the analyses of PAH have been carried out on such phases. Sorbents with RP are also used for the determination of vapour pressures of various PAH by the HPLC method under dynamic conditions.[67] When silica gel is treated with octadecylsilanes, its specific surface diminishes; it has been suggested that the silica gel pores are then not only narrowed but are also frequently blocked by the RP groups.[68]

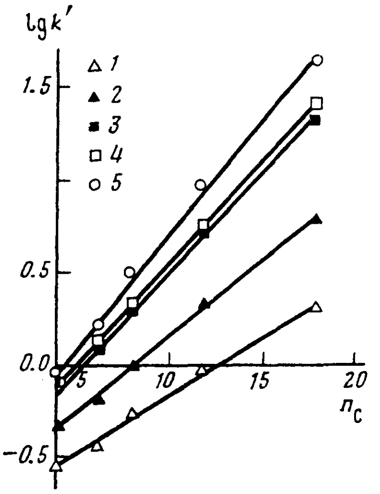


Figure 1. Dependence of the capacity factors of various aromatic hydrocarbons on the length of the chain grafted to the surface of the Spherosil silica gel in an amount of 2.1 μmol m^2 [55] (70: 30 methanol–water mobile phase): *1*) benzene; *2*) naphthalene; *3*) phenanthrene; *4*) anthracene; *5*) pyrene.[55]

Under identical conditions (identical RP composition, eluent flow rate, temperature, and column size), the retention times of PAH on a column with Nucleosil C_{18} are approximately twice as great as on Nucleosil C_8.[21] It is believed that PAH molecules are retained on the bound RP by van der Waals forces and that the bond strength increases with increase of the length of the side chain.

As early as 1973, Sleight[69] derived equations relating the capacity factor and the number of carbon atoms in both unsubstituted and substituted PAH; the methanol–water system was used as the MP. For unsubstituted PAH, the relation is linear along the section from benzene to benzopyrene isomers and is described by the equation

$$\lg k' = a + bC_N\ , \tag{5}$$

where k' is the capacity factor, C_N is the number of carbon atoms in the molecule, and a and b are constants. The introduction of alkyl substituents into the PAH molecule entails an appreciable increase in the retention of the component. This relation is characteristic not only of alkylbenzenes but also of alkylnaphthalenes and alkylphenanthrenes and is likewise described by a linear equation.[69]

Attempts to find correlations between the retention parameters of PAH on ODS phases and the composition and structure of the adsorbate have been made.[70–73,99] Thus a relation has been found[73] between the retention parameter and the geometry of the sorbed molecules for 84 alkylated and non-alkylated PAH. The ratio L/B, where L is the length and B width of the rectangle into which the PAH molecule can be "inscribed" taking into account the bond lengths and the covalent radii of the atoms, served as the criterion for the estimation of sorbability. In almost all cases the elution sequence of the isomeric PAH could be predicted with the aid of this relation: the retention increases with increase of the ratio L/B.

In order to estimate the retention of PAH on RP, the relation between the capacity factors k' and molecular binding χ, taking into account the steric structure of the PAH molecule and the bond orders, has also been employed.[75] The correlation factor F,[74,75] which takes into account the number of double bonds and the number of primary and secondary carbon atoms, has likewise been used to predict the chromatographic properties of the PAH determined. The factors F and χ have been calculated for 34 alkyl-substituted and partly reduced PAH.[75] It has been shown that the retention indices calculated on a computer taking into account these and other parameters can be used to predict the chromatographic behaviour of unknown PAH.[76]

A definite relation has been observed[77] between the retention and the physical properties of PAH. For columns containing different RP, the type of molecules, their structure, and their hydrophobic properties are of the main importance.

Table 1. Thermodynamic characteristics of the sorption of various PAH.

No.	Substance	$-\Delta H^0$, kJ mol^{-1}	$-\Delta S^{0*}$, J mol^{-1}K^{-1}
	Group A		
1	*o*-Terphenyl	8.3	17
2	Anthracene	16.0	43
3	*m*-Terphenyl	11.3	25
4	Fluoranthene	16.9	44
5	1,1-Binaphthyl	13.3	30
6	Triphenylene	18.9	48
7	Chrysene	23.5	62
8	1,3,5-Triphenylbenzene	12.5	23
9	4-Methylpyrene	21.8	55
10	9,10-Dimethyl-1,2-benzoanthracene	21.6	52
11	3,4-Benzofluoranthene	26.6	68
12	9,10-Diphenylanthracene	16.6	32
13	1,2,5,6-Dibenzoanthracene	30.7	79
	Group B		
14	*p*-Terphenyl	18.3	47
15	2,3-Benzofluorene	18.5	47
16	Bifluorenyl	18.0	45
17	1-Phenylnaphthalene	13.1	33
18	3-Methylphenanthrene	14.2	35
9	4-Methylpyrene	21.8	55
19	3-Methylpyrene	21.6	55
20	1,2-Benzoanthracene	22.4	59
	Group C		
21	2-Phenylanthracene	25.4	66
22	2,2′-Binaphthyl	21.9	55
23	9-Phenylanthracene	15.2	35
24	4,4′-Dimethylbiphenyl	14.4	36
25	2-Phenylnaphthalene	15.5	40
26	1-Benzylnaphthalene	10.8	27
27	Phenanthrene	13.3	35
28	Biphenyl	9.1	25
29	Naphthalene	13.3	40

*The entropy changes have been calculated under conditions such that V_S is equivalent to the volume of the sorbent in the column.

The elucidation of the mechanism of the retention of PAH on ODS phases has been prevented by the fact that until recently it was fairly difficult to follow the degree of surface coverage of the sorbent by the reversed phase; as a result, together with the RP monolayers, polymolecular layers appeared, which actually led to the reversal of the elution sequence of PAH from the column.[78-80] Sorbents with identical types of grafted phases can differ appreciably in their selectivity even if they have been manufactured in the same factory.[81,82] New generation sorbents, namely ODS-3, are almost free from the above disadvantages.[83] The influence of the degree of coverage of the sorbent by the reversed phase on the separation of the PAH can be seen in relation to the retention of the isomeric 1,2-benzoanthracene–1,2-benzophenanthrene pair. On monolayer reversed phases, 1,2-benzophenanthrene is eluted before 1,2-benzoanthracene, while on polymolecular layers the reverse order obtains. For pairs such as anthracene–phenanthrene, pyrene–fluoroanthene, and 1,2-benzopyrene–1,2-benzoanthracene, the separation factors α increase on passing from monolayer to polymolecular layer RP.[58]

The characteristics of the retention of PAH on columns with different degrees of coverage of the sorbent by ODS groups differ significantly. Thus, on a monolayer column with an ODS phase, polyphenylarenes are retained more strongly than condensed PAH.[73,78] It has been shown[84] that two series-connected columns filled with sorbents having different ODS group contents on the surface exhibit the same selectivity in relation to PAH as columns filled with mixed ODS sorbents at different concentrations. Data on the retention of PAH on C_{13} RP, grafted to silica gel,[85-90] surface-porous materials,[85,91,92] porous glass,[86] etc.[93-95] are available in the literature.

The retention of unsubstituted PAH and their homologues is influenced significantly by the composition of the MP,[96] which actually makes it possible to alter the elution sequence of the components (Table 1).[69] In studies with reversed phases, the methanol–water and acetonitrile–water systems are usually employed.[97] In certain cases the separation of complex PAH mixtures and individual pairs, for example, 1,5-naphthalenophanes,[103] is improved by modifying the mobile phase by additives containing sodium sulphonates and perchlorates[98,100] or silver ions (0.001–0.02 M);[101,102] the silica gel surface is treated with cetyltrimethylammonium bromide.[104]

With the increase of temperature, not only are the peaks narrowed but the duration of analysis is reduced. The use of a temperature gradient also makes it possible to separate substances eluted under isothermal conditions in the form of one peak and for certain pairs of compounds the reverse elution order is observed. With increase of the separation temperature, the retention of more condensed PAH diminishes at a higher rate compared with less condensed PAH.[105] The use of plots of the relation $\ln K = f(1/T)$ and of the Gibbs equation permits the calculation of the entropy and enthalpy factors and the estimation of their contributions to the overall retention and the sorption mechanism:

$$\Delta G^0 = -RT \ln K = -RT \ln \frac{c_s^x}{c_m^x} = -RT \ln \frac{V_r - V_m}{V_s}, \qquad (6)$$

where ΔG^0 is the free energy of the transfer of the sorbate between the phases, K the partition coefficient assumed equal to the equilibrium distribution constant, c_S^x the concentration of the sorbate X in the adsorbent, c_m^x the concentration of the sorbate X in the MP, V_r the retention volume, V_m the "dead" volume, and V_S the overall volume of the stationary phase or the overall surface area of the sorbent.

Data obtained using silica gel for grafted ODS groups and the 80:20 acetonitrile–water MP are presented in Table 1.[105] The negative enthalpy changes indicate a high probability of the transition of the sample from the MP to the sorbed state. The absolute entropy change increases with increase of adsorbability. For more condensed PAH, a more rigorous elution sequence on the column is observed. With increase of temperature, the entropy differences become dominant, which alters significantly the partition coefficients of the PAH. Thus the components of the pairs separated with appreciably different entropies (Table 1, group A) are eluted in the reverse sequence, while for components in group B with similar or identical entropies, the usual elution sequence is obtained. We may note that, in order to separate components 18, 23, and 27 (Table 1), characterised by identical ΔS^0 but different ΔH^0, the "enthalpy" factor assumes a decisive role. On the other hand, for components 5, 27, and 29 with identical ΔH^0, one may postulate the "entropy" mechanism of the separation process. The separation of a mixture of components with different thermodynamic parameters is determined by the relative contributions of the factors indicated. In this case it is extremely difficult to predict beforehand the results of the chromatographic separation.

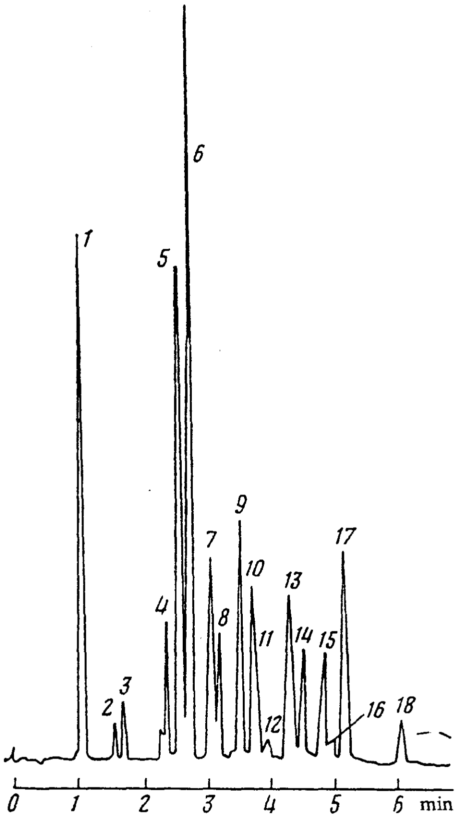


Figure 2. Separation of PAH on a column (125 cm × 4.6 mm) filled with the μ-Bondapak C_{18} sorbent (5 μm) (acetonitrile–water mobile phase; linear concentration gradient of 60–100% of acetonitrile in water over a period of 5 min; eluent flow rate 4 ml min^{-1}; UV detector, 254 mm):[121] *1)* benzene; *2)* admixture; *3)* naphthalene; *4)* fluorene + acenaphthene; *5)* phenanthrene; *6)* anthracene; *7)* fluoranthene; *8)* pyrene; *9)* 3,4-benzofluoranthene; *10)* chrysene; *11)* 1,2-benzanthracene; *12)* admixture; *13)* 1,2-benzopyrene + perylene; *14)* 3,4-benzopyrene; *15)* 1,2,5,6-dibenzoanthracene; *16)* 1,2,3,4-dibenzoanthracene; *17)* 1,12-benzoperylene + 2,3-o-phenylenepyrene; *18)* coronene.

The selection of the composition of the mobile phase and temperature plays an important role in the optimisation of the PAH separation process.[126] By virtue of their exceptional stability, columns with bound RP are widely used in the analysis of PAH by HPLC. The PAH present in carbon black, with molecular weights up to 448, have been successfully separated on such columns.[106] It has been shown that alkylnaphthalenes can be analysed on carbon black.[107] Examples of the gradient elution of PAH mixtures have been fairly widely described in the literature. By altering the composition of their MP, it is possible to achieve not only an acceptable separation and retention but also a change in the elution sequence. With increase of the content of the organic component in the MP, PAH having increasingly higher molecular weights are eluted.[108,109] Both linear and non-linear gradients have been used. The advantages of the employment of the gradient technique in the analysis of PAC have been demonstrated in a number of studies.[110,111,112] For the effective separation of heavy PAH with a molecular weight up to 450, the tetrahydrofuran–acetonitrile–methanol–water four-component gradient system has been proposed.[113]

The separation of PAC on the high performance Vydac 201 TP, C_{18} column (linear gradient; acetonitrile–water MP) has been carried out.[78] The same composition of the MP under gradient conditions has been used for the separation of a model mixture of PAH ranging from coronene to bicoronyl on a column containing Nucleosil 5 C_{18} [114] and also for other PAH mixtures.[115–119] A gradient anhydrous MP, for example a methylene chloride–acetonitrile mixture, can sometimes be usefully employed for the analysis of PAH.[120] The gradient elution of a mixture containing 18 different PAH is illustrated in Fig. 2.[121]

A programmed variation of the flow rate or temperature is sometimes used to improve separation.[21] However, the latter exerts a significantly smaller influence on the retention parameters in liquid chromatography than in gas chromatography.

High resolution chromatography on RP can be readily achieved with gradient elution and the rapid return of such columns to the initial equilibrium and the rapid change to the new composition of the MP makes them very convenient to operate.

The separation of high-molecular-weight PAH in both the normal and reversed phase variants requires a careful selection of the MP. In many studies using isocratic and gradient elution, it has been possible to separate PAH with molecular weights of 400–600.[122–124]

2. Separation on Sorbents with Grafted Polar Groups

Sorbents with grafted polar groups (SGPG) are being increasingly used for the separation of PAH. The groups in alkyl(aryl)silanes, used to modify the surfaces of classical sorbents, contain one or several polar groups (NH_2, NO_2, OH, CN, etc.). The bound organic layer of polar stationary phases is monomeric because the mass transfer across the layer proceeds at a high rate and the mass transfer along the layer becomes minimal. By selecting SGPG with different functional groups, it is possible to vary widely the sorption characteristics.[125] In other words, the separation on SGPG combines the advantages of partition and sorption chromatography. The concentration of functional groups on the silica gel surface is as a rule 3–4 group on 100 Å.[126] The properties of various polar phases suitable for the separation of PAH have been compared.[127]

The mechanism of the retention of PAH on SGPG is fairly complex. Here one must take into account the interaction between the π-electron systems of the sample components and various structures on the polar surface.[128] Unsubstituted PAH are eluted in order of increasing molecular weight[129] and ponents which cannot be separated on a non-polar RP.[130]

The characteristics of the retention of more than 90 unsubstituted and alkyl-substituted PAH on a polar phase containing amino-groups have been described.[78] It was noted that the retention of the PAH increases with increasing number of aromatic nuclei in the molecule. In contrast to the usual columns with RP, the presence of alkyl groups in the PAH molecules influences only insignificantly the retention sequence, which makes it possible to use the above phase for preliminary fractionation in the analysis of complex mixtures. Furthermore, the use of volatile non-polar MP facilitates the concentration of the collected fractions.

The separation of PAH on a polar phase containing aminopropyl groups has been investigated.[131,132] The non-polar MP were cyclohexane and the polar phases were methanol–water or acetonitrile–water mixtures. In the former cases the separation was attributed to the interaction of the unshared electron pair of the N atom and the π-electrons of the PAH and in the latter to the partition effect due to the employment of MP of high polarity and the mixed adsorption-partition effects in MP with a lower polarity.

A complex mixture of aromatic hydrocarbons and alcohols, which included also naphthalene and anthracene, has been successfully separated[133] on a column with aminated Lichrosorb.

The retention parameters of 32 PAH on the usual columns with silica gel and on columns with SGPG have been compared[134] and considerable differences in the retention volumes and capacity coefficients have been detected. According to the authors, the cyclic amide SGPG phase interacts with the PAH via both the normal-phase and reversed-phase mechanisms, exhibiting at the same time specific features in the separation process. This results in a significant change in the separation factors for the individual pairs and in the elution sequence of the components. Thus, on a normal-phase sorbent, 9,10-diphenylanthracene and phenanthrene emerge as a single peak, while on SGPG these compounds are separated (the selectivity was 3), phenanthrene emerging first.

PAH have been analysed on grafted phases containing nitrile, diol, ethyl, quaternary ammonium, and amino- and diamino-groups.[135,136,296] The phase with diamino-groups proved to be the most selective. The use of a system comprising two columns—one with a polar phase and another with a non-polar phase—is even more promising for the study of complex PAH mixtures.[137] The characteristics of the separation of a number of PAH, their nitrogen-containing analogues, and biaryls have been investigated[71] on silica gel modified with polar nitrophenyl groups. For each of these groups of compounds analysed, a linear relation was observed between the logarithm of the retention of the components and the number of carbon atoms in the molecule. Furthermore, the PAH were readily separated from their nitrogen-containing analogues owing to the greater polarity of the latter. In a number of studies Nucleosil 100-5 NO_2 has been used successfully for the analysis of heavy PAH.[138–140]

Blumer et al.[141] separated coal tar on a nitrophenyl phase into more than 100 components. In contrast to capillary gas chromatography, where only 30% of the composition of the resin can be determined, on the nitrophenyl phase up to 70% of the composition has been isolated by the HPLC method. Using the nitrophenyl phase, it has been possible to separate PAH of complex composition with molecular weights up to 600.[122] It has been found[142] that, under HPLC conditions, the nitrophenyl phase is preferable for the analysis of PAH present in dust to the amine phase and RP C_{18}. The characteristics of the retention of PAC on the nitrophenyl phase have not so far been investigated in detail.

Phases with other polar groups, for example, nitrofluoreneimine,[143,144] picramidopropyl,[145] 3-(2,4-dinitroanilino)-propyl,[146] and phthalimidopropyl[147] groups, are also suitable for the separation of PAH. With the aid of the last phase, 1,12-benzofluoranthene and perylene were separated and the reverse elution sequence of the components of the binary 3,4-benzopyrene–1,2-benzopyrene mixture was noted compared with the C_{18} phase. Stationary SGPG phases, forming charge-transfer complexes with PAH, are entirely suitable for the separation of complex PAC mixtures into di-, tri-, and poly-aromatic compounds.[148]

Studies of the relation between the capacity factor k' and the molecular structure of PAH have been published.[149,313,318] A sufficiently distinct regularity in the deviation of the k' (Table 2) on passing from different silica gels with grafted phases to pure silica gel has not been observed on phases of different polarity in the separation of a number of PAH. Examination of the selectivity in relation to pairs of compounds difficult to separate has also revealed a scatter of the relevant values. For example, in the separation of the anthracene–phenanthrene pair the selectivity assumes values from 0.94 to 1.46, while for the anthracene–fluorene pair it ranges from 1.09 to 2.30, etc. The use of other factors (F and L/B) for the calculation of the capacity factor is fruitful when these are present simultaneously in an equation of the type

$$k'=aF+b(L/B)+c\ , \qquad (7)$$

where F = number of double bonds + number of primary and secondary carbon atoms—0.5 (for a non-aromatic nucleus) and a, b, and c are column constants.

Table 2. Characteristics of the retention of PAH on various stationary phases.[149]

Substance	F	L/B	Capacity factor, k'						
			C_2	C_p	C_8	C_{18}	S_{N_1}	S_{N_2}	S
Benzene	3.0	1.10	1.89	2.00	1.48	1.05	0.48	0.19	0.48
Naphthalene	5.0	1.24	3.01	3.55	2.22	1.67	1.42	0.50	1.06
Fluorene	6.5	1.57	4.40	5.29	2.89	2.44	2.68	0.76	1.92
Acenaphthylene	5.5	1.08	3.35	4.24	2.49	2.03	2.58	0.93	1.48
Anthracene	7.0	1.57	4.81	6.27	3.36	3.20	3.47	1.75	2.16
Phenanthrene	7.0	1.46	4.49	5.86	3.14	2.99	3.68	1.20	1.70
Pyrene	8.0	1.27	5.56	7.47	3.80	3.97	5.55	1.68	2.40
Fluoranthene	8.0	1.27	5.59	7.42	3.80	3.97	5,55	1.68	2.40
Chrysene	9,0	1,72	7.13	10.4	4.88	5.93	9.03	2,50	3.44
Naphthacene	9.0	1.89	8.28	11.4	5.27	7.18	8.71	2.54	3.31
Triphenylene	9.0	1,12	6.45	9.34	4.67	5.48	9.19	2.63	3.11
3,4-Benzopyrene	10.0	1,50	9.06	13.8	6.75	9.86	11,8	3.70	3.98

Notation: C_2 = dimethylsilica gel, C_p = phenylsilica gel, C_8 = octylsilica gel, C_{18} = octadecylsilica gel, S_{N_1} = Fine SIL-NH_2, S_{N_2} = Lichrosorb-NH_2, and S = pure silica gel.

A reliable method for predicting the parameters of the chromatographic retention of various PAH has been proposed;[256] a high correlation coefficient (0.97–0.99) was obtained in all cases. The authors began with the fact that the logarithm of the capacity factor of the molecule can be represented as the sum of the logarithms of the capacity factor of its constituent fragments. The method is suitable for any type of chromatographic separation (adsorption, partition, or a mixed type). For the majority of PAH, the calculated capacity factors are satisfactorily correlated with experimental data over a wide range of polarities of the mobile and stationary phases. The isomeric 2,7- and 2,6-dimethylnaphthalenes are exceptions, but this in no way reduces the advantages of the new method, which can be extended to PAH derivatives after the appropriate correction of the calculated data.

IV. THE APPLICATION OF MICROPACKED AND CAPILLARY COLUMNS FOR THE ANALYSIS OF PAH

The increase of the molecular weight of PAH leads to a rapid increase of the number of isomers, which requires the application of high performance columns and a more careful selection of the MP. The efficiency of the system can be increased by connecting several columns in series.[151] However, this entails an increase of the pressure drop and of the duration of the analysis. Furthermore, a large pressure drop entails the heating of the silica gel particles owing to friction, which leads to additional spreading of the peak.[150]

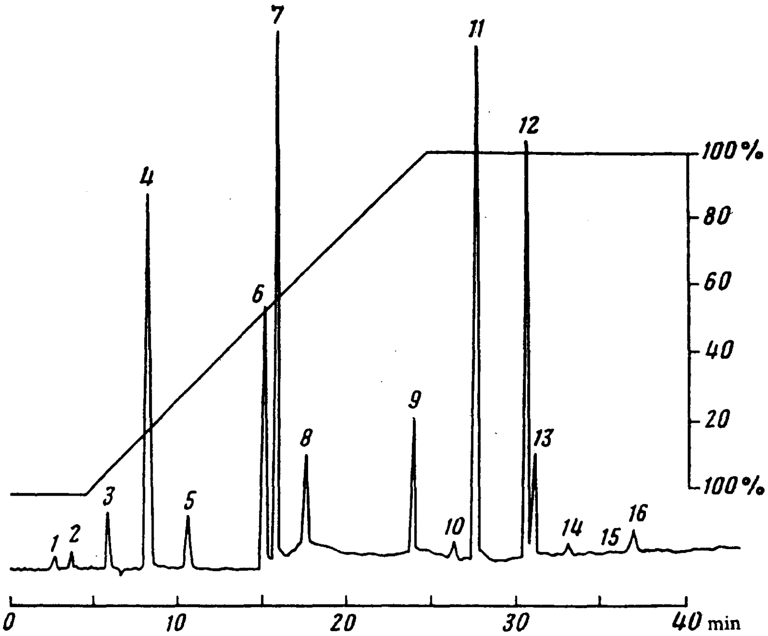
Micropacked, capillary, and microcapillary columns are being increasingly used nowadays for the analysis of complex PAH mixtures. These columns have a number of advantages, which include (1) the possibility of employing a combination of a chromatograph with a mass-spectrometer or a flame-ionisation detector, (2) high efficiency (more than 10^5 theoretical plates), which permits the separation of extremely complex mixtures, (3) a decrease of the consumption of the MP by a factor greater than 20, which permits a much wider use of expensive and toxic solvents, (4) an increase of the sensitivity of the determination of the components by a factor greater than 20, and (5) the need for very small amounts of the specimen in the analysis (less than 1 μl). Microcolumn liquid chromatographs, with the aid of which it is possible to solve a wide variety of research and technical problems, have received wide recognition in our country and abroad. Soviet investigators have used successfully the Ob'-4 and Milikhrom chromatographs for the analysis of PAC.[152]

Packed microcolumns are quite efficient. For example, a 1 m × 1 mm column filled with Partisil ODS/10 μm has an efficiency up to 30 000 theoretical plates (t.p.). A complex mixture of PAH extracted from coal has been separated on this column.[312] A battery of 14 series-connected columns of this kind has an efficiency of 650 000 t.p.[153] A multicomponent mixture of PAH has been separated on 100 × 0.12 mm and 100 × 0.340 mm ultramicrocolumns filled with ODS SC-01 silica gel.[154,155]

Capillary packed columns have an even greater efficiency,[156] which is calculated from the relation $H \leq 3d_p$ (d_p is the particle diameter). Thus the efficiency of a 1 m× 320 μm column filled with ODS silica gel (particle size 3 μm) is 110 000 t.p.; a 2 m × 300 μm column with the same filler has an even greater efficiency—144 000 t.p. (with respect to pyrene for k' = 10). Both columns have been used successfully for the identification of PAC contaminating the environment.[153,157]

A capillary column whose inner surface has been treated with silicone SE-30 proved to be highly efficient for the analysis of a model mixture of PAH.[158,308] The heavy aromatic fraction of coal tar has been separated[159-161] on a 55 m × 70 μm column filled with alumina (particle size 30 μm) having grafted ODS groups. The use of a glass capillary column on the inner surface of which a layer of silica gel modified by cetyltrimethylammonium bromide has been deposited[162,310] is also promising. The separation of PAH on such a column proceeds similarly to the separation on a capillary column with grafted ODS groups.

In order to reduce the duration of analysis, it is useful to employ gradient elution for the separation of PAH having a complex composition.[163,164,311] An example of such separation on a packed capillary column is illustrated in Fig.3.



3. Gradient separation of PAH on a 66 cm × 250 μm column filled with Vydoc 201 TP silica gel (5 μm).[163] The variation of the composition of the MP during analysis is shown above: *A*) 65% acetonitrile + 35% water; *B*) 80% acetonitrile + 20% dimethoxyethane. Sample composition (the amount in ng is given in brackets): *1*) naphthalene (20); *2*) acenaphthylene (4); *3*) acenaphthene (20); *4*) fluorene (4); *5*) phenanthrene (2); *6*) anthracene (2); *7*) fluoranthene (4); *8*) pyrene (2); *9*) 1,2-benzoanthracene (2); *10*) chrysene (2); *11*) 3,4-benzofluoranthene (4); *12*) 1,12-benzofluoranthene (2); *13*) 3,4-benzopyrene (2, detectable minimum amount 50 pg); *14*) 1,2,5,6-dibenzoanthracene (4); *15*) 1,12-benzoperylene (4); *16*) 2,3-*o*-phenylenepyrene.

Microcolumns and capillary columns with MP of different polarity have been used to separate PAH in supercritical (fluid) chromatography. Hydrocarbons (pentane, butane, and isobutane), dimethyl ether, carbon dioxide, nitrous oxide, etc. have been used as the MP. Multicomponent PAH mixtures[166–168] as well as the PAC present in soot,[306] in the exhaust gases of automobiles,[169] and in coal tar[170] have been successfully separated with the aid of microcolumn liquid chromatography.

Despite their evident advantages, capillary columns are being fairly slowly introduced into chromatographic practice. The reasons are failure to develop as yet a reproducible method for the preparation of these columns, the absolute need for a new system for the introduction of the sample, inadequately improved pumps working at very high pressures, and, in addition, the need for very small flow cells in the detection of the components, for which one can usefully employ the "tail" section of a glass column. Micropacked columns are extremely promising.[171,172]

V. DETECTION SYSTEMS

The principal advantages of the analysis of PAH by the HPLC method are due to the possibility of employing highly sensitive and selective detectors. The molecules of aromatic compounds are known to be capable of absorbing ultraviolet light and certain PAH exhibit an intense fluorescence. Detectors working in accordance with the above principles have come to be widely used in the analysis of PAH by liquid chromatography.[173] Aromatic solvents cannot be used as MP, but this does not create difficulties in the selection of the eluent. There are fairly numerous different solvents which exhibit a minimal absorption at the wavelength employed for detection.

1. Ultraviolet Detectors

Although various PAH and their analogues differ somewhat in the absorption of UV light at fixed wavelengths, the detection of substances in amounts not exceeding several nanogrammes is quite feasible. The use of UV spectrophotometers permits the selection of the optimum wavelength for the detection of specific components of PAH.[174] A UV detector with a variable wavelength is quite often used to increase the selectivity.[175–177] The complete UV spectra have been used[114] to identify PAH after separation by HPLC. For analysis, it is useful to measure the relative absorption of PAH at several wavelengths.[178,179] The advantages of UV scanning with stopped flow for identification of PAH peaks have been demonstrated.[180,181] By altering the wavelength in the UV region it is possible to control successfully the content of, for example, 3,4-benzopyrene in the presence of perylene at 290 nm or of pyrene in the presence of fluoranthene at 360 nm.[175] Detection with a variable wavelength under the conditions of reversed phase separation[182] make it possible to detect fairly readily 3,4-benzopyrene in coal tar.

In order to determine the maximum number of components, it is useful to employ rapid scanning and multi-wavelength detectors[183–185] with Fourier transformation.[186] The sensitivity of the determination of PAH can be increased by using weakly pulsating pumps. Pumps of the syringe type which do not give rise to pulsations in the flow are best for this purpose.[187]

Definite information can be obtained by using two combined detectors tuned to different wavelengths[188,189] and also by combining UV detectors with a fluorimetric detector.[190–192] The sensitivity of the determination of PAH can be increased with the aid of a detector based on the use of the Cherenkov effect,[193], etc,[194–197]

2. Fluorimetric Detectors

The rapid growth of the manufacture of fluorimetric detectors for HPLC is due to their selectivity with respect to condensed PAH[198,199] and high sensitivity.[173,200,201] The analysis of admixtures whose amount does not exceed 10–100 pg then becomes entirely realistic. It is believed[202–204] that PAH detection limits below 10^{-12} M are entirely attainable when laser-excited fluorescence is employed. At the same time the use of fluorescence detection can sometimes lead to inaccurate estimates of mixture compositions, because the signal intensities at different wavelengths are not the same. Under these conditions, the signals of a series of PAH components can diminish appreciably and can even disappear.[205]

Fluorimetric filters and spectrofluorimeters are used to determine PAH in air-borne dust,[176] in the exhaust gases from diesel engines,[204] in cigarette smoke,[206] and in various petroleums and oils.[207–209] The fluorescence peak intensity rations under different conditions of the excitation of the fluorescence have been used to identify 17 different PAH present in food, water, and tobacco smoke.[210]

In certain studies attempts have been made to improve the technique of the fluorimetric detection of PAH in systems in the environment.[211–214] In particular, the use of a narrow-band filter greatly improved the sensitivity of the determinations of the readily separated PAH; however, for poorly separated peaks, the best results are given by a monochromator.[211] A two-photon laser fluorescence detector[215–217] and a detector based on β-induced fluorescence[218] have been used successfully to analyse various asphaltenes.

The sensitivity of a fluorescence detector increased significantly when an MP with added dodecyl sulphate was used.[219] The selective extinction of the fluorescence of certain PAH in the presence of nitromethane has been investigated.[198,220,221] The addition of 0.5% of nitromethane to the MP significantly extinguishes the fluorescence of non-fluoranthene PAH (the fluorescence of anthracene is not fully extinguished).[220]

Table 3. Conditions in the analysis of PAH contained in various objects within the environment.

Object of analysis	Sorbent	Composition of mobile phase	Detector	References
Petroleum	Bio-Sil ODS-10	methanol - water, G	UV	[257]
Petroleum	Spherisorb C_{18}	methanol - water (80 : 20)	F	[258] ([230, 259, 260])
Petroleum, shale, coal liquefaction products	Chromegabond $(NH_2)_2$	hexane - methylene chloride, G	UV	[261]
Ditto	Woelm alumina	hexane - methylene chloride, G	UV	[261]
"	2,4-dinitroanilinopropylsilica gel	hexane - methylene chloride, G	UV	[261]
Bitumens, motor oils	Partisil 5	hexane	UV	[262] ([263])
Ditto	Corasil C_{18}	methanol - water (75 : 25)	UV, F	[264] ([265])
Heavy petroleum fractions, coal tar	Nucleosil NO_2, NH_2, CN, SA, Lichrosorb Si 60, Alox T; Spherisorb A5U	hexane; hexane - methylene chloride, G	UV	[266] ([304])
Coal tar, pitch	Lichrosorb, μPorasil	cyclohexane	UV	[182]
Ditto	μBondapak, C_{18}	acetonitrile - water (60 : 40)	UV	[182]
Coal tar	alumina C_{18}	acetonitrile, acetonitrile - dichloroethane, G	F	[160] ([307])
Coal pitch	Lichrosorb RP-8	water - acetonitrile - dimethylformamide, G	UV	[123]
Ditto	Nucleosil 100-5NO_2	hexane - chloroform, G	UV	[140] ([267])
Coal tar and petroleum processing products	HC-ODS	tetrahydrofuran-acetonitrile (70 : 30)	UV, F	[268]
Ditto	PAH/10	acetonitrile - water, G	F	[268] ([31, 191])
Coal liquefaction products	μBondapak, C_{18}	methanol - water (65 : 35)	UV	[74, 269]
Ditto	Partisil PXS 10/25 ODS	acetonitrile - water (70 : 30)	F	[203] ([239, 240, 270, 271, 317])
PAC hydrogenation products	Lichrosorb RP-18	methanol - water, G	UV	[272]
Tobacco smoke	Micropak C-H "Varian"	methanol - water, G	UV	[6]
Air contaminants	Vydac 201 TP	acetonitrile - water (70 : 30)	F	[273]
Ditto	Fine SIL C18-10	acetonitrile - water (70 : 30)	F	[274]
"	Lichrosorb NH_2	iso-octane	UV	[142]
"	Nucleosil 5 NO_2	iso-octane - methylene chloride (9 : 1)	UV	[142]
"	Lichrosorb RP-18	acetonitrile - water (85 : 15)	UV	[142] ([9, 81, 118, 119, 176, 187, 192, 205 - 281])
Water contaminants	Lichrosorb RP-18	methanol - water (85 : 15)	F	[282]
Ditto	PAC 254-400 "Contron"	methanol, acetonitrile	UV	[283]
"	Perkin-Elmer HC-ODS	acetonitrile - water, G	UV	[201]
"	Perkin-Elmer HC-ODS	aqueous solution of acetonitrile (38%) and methanol (15%)	F	[284]
"	μBondapak C_{18}	acetonitrile - water (80 : 20)	F	[285] ([286-290, 309])
Deposits on sea bottom, marine organisms	Lichrosorb RP-18	acetonitrile-water, G	UV	[291] ([292-295])
Exhaust gases from engines	Lichrosorb RP-18	acetonitrile-water (80:20)	UV	[296]
Ditto	Zorbax TM ODS	methanol-water (8:1)	F	[85]
"	Spherisorb ODS	methanol-water, G	UV	[297] ([250, 298-300, 316])
Automobile fuel	Fine SIL C_{18}-10	acetonitrile-water (80:20)	F	[302]
Barley malt	Zorbax ODS	methanol-acetonitrile-water, G	UV, F	[303]

Notation: G = gradient elution, UV = ultraviolet detector, F = fluorimetric detector. The additional literature relevant to the object of analysis is indicated in round brackets.

Only the peaks of PAH of the fluoranthene series, namely fluoranthene, 3,4-benzofluoranthene, and 11,12-benzofluoranthene, remain on the chromatogram (Fig.4). The addition of a fluorophor, for example, aniline, to the MP makes it possible to detect both fluorescent and non-fluorescent PAH.[222]

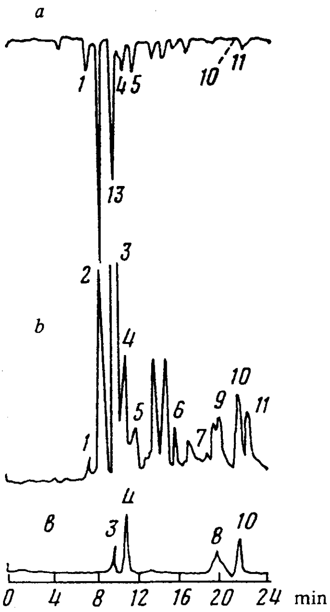


Figure 4. Separation of an extract from coal tar on a reversed phase: *a*) detection at 254 nm; *b*) fluorescence detection; *c*) detection with fluorimetric quenching (0.5% of nitromethane in the MP).[200] Column filled with Vydoc 201 TP silica gel (10 μm); mobile phase—linear gradient of 50—100% of acetonitrile in water over a period of 25 min; eluent flow rate 2 ml min^{-1}. Sample composition: *1*) fluorene; *2*) phenanthrene; *3*) anthracene; *4*) fluoranthene; *5*) pyrene; *6*) 10,11-benzofluoranthene; *7*) 1,2-benzopyrene; *8*) 3,4-benzofluoranthene; *9*) perylene; *10*) 11,12-benzofluoranthene; *11*) 3,4-benzopyrene.

Multichannel rapidly scanning spectrometers have been employed[223] for the detection of eluates containing PAH, for example, for the determination of the origin of oil slicks.[223] A fluorimetric detector combined with computer techniques and a data bank has been used successfully for the analysis of complex PAH mixtures.[224] The employment of a rapidly scanning device with a photodiode detector and a computer is promising for the optimisation of the composition of the MP.[314]

3. Other Detection Methods

The HPLC and mass-spectrometric methods have been combined successfully in recent years for the separation and identification of complex PAH mixtures.[225–231] This approach proved to be fruitful for the analysis of both model mixtures[154, 232–236] and coal liquefaction products containing heavy aromatic hydrocarbons.[237–240]

Various ionisation procedures which make it possible to differentiate isomeric PAH are used to detect mass-spectrometrically the PAH eluted from the column, namely electron impact, chemical ionisation, and, much more rarely, field ionisation and field desorption. The reliability of the method is determined both by the selection of the ionisation procedure and of suitable masses, which are characteristic for the substances to be determined.[5,241] Detectors employing proton magnetic resonance,[242] IR spectroscopy,[243] and other spectroscopic methods combined with computer techniques[244] and Fourier transformation[186] have also been described.

It is noteworthy that even the use of the most selective and effective columns in the analysis by the HPLC method does not permit the complete separation of isomeric PAH in complex mixtures. For a greater reliability of the data obtained, it is useful to combine HPLC with gas chromatography and mass spectrometry[160,245–251] and also various spectroscopic methods,[6, 252–255] which makes it possible to increase significantly the amount of information derivable from the analytical results.[256]

VI. ANALYSIS OF PAH IN VARIOUS OBJECTS WITHIN THE ENVIRONMENT

Table 3 presents the conditions for the analysis of PAH contained in various objects within the environment. It is seen that the use of adsorption chromatography permits the solution of a very limited range of problems. Furthermore, the long duration of the analytical cycle is a significant disadvantage in routine analyses of complex mixtures.

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It follows from the data described that the separation of PAH on reversed phases grafted to the spherical particles of wide-pore silica gel having a small diameter (3—5 μm) is much more effective (when both non-polar and polar grafted groups and appropriate eluents are employed). Gradient elution can be usefully applied in the study of PAH forming part of the composition of petroleum, coal tar, the products of their processing, and contaminated water and air. Good results have been obtained following the combined application of UV and fluorescence detectors. Computer techniques make it possible to detect, in particular, the UV spectra of individual PAH in the course of chromatographic separation and to compare them with the available information. Methods in which HPLC is used in combination with mass spectrometry, ^{1}H NMR, ^{13}C NMR, and other methods have been developed for the identification of unknown PAH. Computer techniques can then make it possible to reduce to a minimum the time consumed in comparing the data obtained and to increase the accuracy of the analytical determination.

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Detailed Kinetic Mechanism of the Combustion of Homogeneous Gaseous Mixtures with Participation of Oxygen-containing Oxidants

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The kinetic mechanisms of the oxidation and combustion of hydrogen, methane, methyl alcohol, acetylene, ethylene, ethane, and methylamine, using oxygen as well as hydrogen peroxide and nitric acid as oxidants, are discussed. The calculated and experimental data obtained under static conditions, in a flow, during flame propagation, and in shock tubes are compared. The bibliography includes 184 references.

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I. INTRODUCTION

The aim of the present review is a joint examination of the available kinetic schemes for the oxidation of hydrogen, hydrocarbons, and their derivatives, which permit the construction of fairly general detailed kinetic mechanisms (DKM) of oxidation and combustion processes. It has been found that, despite the individual differences between the initial molecules of the fuel and the oxidant, the atomic composition of such molecules is important for the course of the reaction. Depending on this composition, the same or different intermediate species are formed which determine the character of the interaction. Even when all the reaction channels are not know accurately and despite extremely approximate values of the rate constants being frequently employed, it is possible to achieve by computation a fairly satisfactory description of the kinetics of experimental processes.

We may note that, although the questions analysed below are of intrinsic importance, they constitute a small part of the general kinetic theory whose foundations have been laid in a number of fundamental monographs and textbooks (see, for example, Refs. 1–10).

The number of fuels and oxidants used in practice and important for the theory of combustion processes is very large. Fuels having a complex multicomponent composition are usually employed. However, at the present time one may hope to be able to construct detailed kinetic mechanisms only for an extremely limited number of simplest fuel–oxidant pairs, which are the subject of the exposition below. Complex compositions can be modelled by simpler ones but even the latter have frequently a direct practical application.

II. HYDROGEN AND HYDROGEN PEROXIDE

The principal characteristics of the DKM of combustion can be illustrated in relation to the oxidation of hydrogen. The mechanism of the oxidation of hydrogen has become one of the first DKM in the study of which many fundamental postulates of chemical kinetics were developed and tested, including the theory of branched processes.[1,2,6,7,11-19]

Extensive experimental data referring to the oxidation of hydrogen, mainly in the region of the ignition peninsula, and all the known fundamental elementary stages of the process were described, i.e. in essence a DKM had been constructed, already in a monograph of Nalbandyan and Voevodskii[8] and then in the studies of Semenov[1] and Kondrat'ev[7] [Table 1, reactions† (1), (-4), (-6), (7), (-8), (-11), (-14a), and (-83)].

In these studies it is possible to find all the fundamental features of simple and branched chain hydrogen oxidation reactions (as well as the oxidation reactions of hydrocarbons and other combustible substances), including those accompanied by a rise of temperature, and the relevant communications give compilations of numerous experimental and calculated data and comparisons which provide a quantitative justification of the theory. A general solution of many ignition problems can be found with the aid of the following approximate system of equations:[2,7,16]

$$\frac{\mathrm{d}n_j}{\mathrm{d}t}=\sum_i w_{ij} \ , \tag{I}$$

$$\rho C\frac{\mathrm{d}T}{\mathrm{d}t}=\sum_{ij} h_{ij}w_{ij}+\frac{\varkappa S}{V}(T-T_c) \ , \tag{II}$$

where n_j is the concentration of species j, t the time, T the temperature, ρ the density, C the heat capacity, and ω_{ij} and h_{ij} are respectively the rate and heat of reaction in the ith elementary step with participation of the jth component, κ is the coefficient of heat evolution in the wall of the reaction vessel, S and V are respectively the surface and volume of the reaction vessel, and T_c is the temperature of the vessel wall. The usual initial conditions apply: $t = 0$, $n_j = n_{j0}$, and $T = T_0$.

Later communications contain a series of revisions which specify in greater detail the mechanism of the combustion of hydrogen. Thus a mechanism has been proposed[17] for the oxidation of hydrogen under conditions remote from the ignition peninsula, namely under detonation conditions characterised by high temperatures and pressures. For this reason, a number of bi- and tri-molecular processes involving the recombination of active centres, which in this case play a significant role owing to the high concentration of atoms and radicals, have been included in the mechanism [Table 1, reactions (11)–(13), (19), and (83)].

It has been established[18,19] that the mechanism of the ignition reaction of hydrogen–oxygen mixtures, proposed by Nalbandyan and Voevodskii[8] and supplemented by recombination processes of the kind described above is very suitable for the description of the propagation of a laminar flame. This follows from a comparison of the calculated and experimental data for the rate of heat evolution Σhw in the reaction zone at low pressures P (Fig.1). A theoretical basis for such calculations is provided by the system of equations describing the stationary one-dimensional propagation of the flame:[2,7,16]

$$\frac{\mathrm{d}}{\mathrm{d}x}D_j\rho\frac{\mathrm{d}(n_j/\rho)}{\mathrm{d}x}-\rho_0u_n\frac{\mathrm{d}(n_j/\rho)}{\mathrm{d}x}+\sum_i w_{ij}=0 \ , \tag{III}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\lambda\frac{\mathrm{d}T}{\mathrm{d}x}-\rho_0u_n\frac{\mathrm{d}CT}{\mathrm{d}x}+\sum_{ij} h_{ij}w_{ij}=0 \ , \tag{IV}$$

where x is the coordinate of the propagation of the flame, λ the thermal conductivity, u_n the laminar rate of propagation of the flame, ρ_0 and ρ are respectively the initial and current densities, and D_j is the diffusion coefficient of the jth component of the chemical reactions. The boundary conditions at $x = 0$ and $x = 1$ (end of the reaction zone) are as follows:

$$\left(T-\frac{\lambda}{\rho_0u_nC}\frac{\mathrm{d}T}{\mathrm{d}x}\right)\bigg|_{x=0}=T_0;\quad\left(n_j-\frac{\rho D_j}{u_n\rho_0}\frac{\mathrm{d}n_j}{\mathrm{d}x}\right)\bigg|_{x=0}=n_{j0};$$

$$\frac{\mathrm{d}T}{\mathrm{d}x}\bigg|_{x=l}=0;\ \frac{\mathrm{d}n_j}{\mathrm{d}x}\bigg|_{x=l}=0 \ .$$

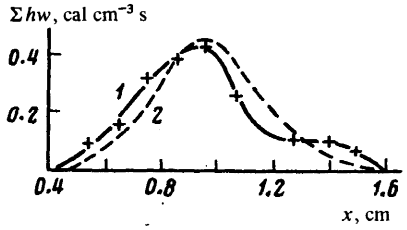

Figure 1. Dependence of the rate of heat evolution on the coordinates in the reaction zone;[19] $[H_2]_0 = 7.2\%$, $[O_2]_0 = 92.8\%$, $T = 295$ K, $P = 0.068$ atm, rate of propagation of the flame $u_n = 19.6$ cm s^{-1}: *1*) experiment; *2*) calculation (here and henceforth volume percentages are quoted).

The rate of heat evolution profile was calculated from the material balance equations (III) in which the terms describing the appearance and consumption of each substance were set up on the basis of the kinetic scheme [Table 1, reactions (1), (-4), (-6), (7), (11), (12), (17), and (28)]. Readings of the non-inertial resistance thermometer on a spherical bomb with central ignition were used to determine $T(x)$.[18]

Here it is necessary to make certain general remarks concerning the rate constants. For certain reactions, these quantities have been frequently measured by different workers and fairly similar results have been obtained. However, frequently there is a large scatter in the experimental values. In such cases (and these are in the majority) it is sometimes difficult to find arguments for the justification of the *a priori* selection of the value of the rate constant and the problem is solved by comparing the calculated data with the results of experiments carried out under different initial conditions. Special attention has been devoted in the present review to such comparisons. Furthermore, we may note that processes corresponding to the exothermic direction of the reaction are regarded as forward processes, while those involving the endothermic direction of the reaction are regarded as reverse processes. Strictly speaking, it is necessary to take into account all the forward and reverse processes. However, in each specific calculation one needs to consider only those which contribute appreciably to the development of the process.

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† Here and henceforth M is any third species removing or supplying energy; the minus sign refers to the reverse reaction.

Table 1. Combustion mechanisms.

No. of reaction	Reaction	h, kcal mol^{-1}	Forward reaction			Reverse reaction		
			A, mol litre^{-1}s^{-1}	E, kcal mol^{-1}	Refs.	A, mol litre^{-1}s^{-1}	E, kcal mol^{-1}	Refs.
1	$OH+H_2\rightleftarrows H+H_2O$	15	$2.4\cdot10^{10}$	5.2	[20]	$1.14\cdot10^{11}$	20.4	—
4	$OH+O\rightleftarrows H+O_2$	17	$4.16\cdot10^{9}$	—0.78	—	$7.8\cdot10^{10}$	15.9	[21]
6	$OH+H\rightleftarrows O+H_2$	2	$6.9\cdot10^{9}$	7.04	—	$1.5\cdot10^{10}$	8.9	[22]
9	$OH+OH\rightleftarrows O+H_2O$	17	$1.44\cdot10^{10}$	0	[23]	$1.51\cdot10^{11}$	17	—
11	$H+H+M\rightleftarrows H_2+M$	103	$3.6\cdot10^{9}$	0	[24]	$1.74\cdot10^{13}$	105	—
12	$O+O+M\rightleftarrows O_2+M$	118	$1{,}8\cdot10^{9}$	0	[25]	$7.4\cdot10^{13}$	120	—
13	$OH+H+M\rightleftarrows H_2O+M$	118	$3.6\cdot10^{10}$	0	[24]	$8.3\cdot10^{14}$	120	—
19	$O+H+M\rightleftarrows OH+M$	101	$1.44\cdot10^{10}$	0	[17]	$3.1\cdot10^{18}$	104	—
83	$OH+OH\rightleftarrows H_2+O_2$	19	$6\cdot10^{7}$	20.4	—	$2.5\cdot10^{9}$	39	[26]
17a	$H+HO_2\rightleftarrows H_2+O_2$	56	$6\cdot10^{9}$	0	[27]	$1.1\cdot10^{10}$	56	—
7	$H+O_2+M\rightleftarrows HO_2+M$	47	$4.14\cdot10^{9}$	0	[28]	$5.7\cdot10^{12}$	48.8	—
17	$H+HO_2\rightleftarrows OH+OH$	37	$2\cdot10^{10}$	0	[29]	$1{,}62\cdot10^{9}$	37.6	—
26	$O+HO_2\rightleftarrows O_2+OH$	54	$6\cdot10^{10}$	0	[28]	$9{,}43\cdot10^{10}$	54	—
27	$OH+HO_2\rightleftarrows O_2+H_2O$	71	$6\cdot10^{9}$	0	[30]	$9.9\cdot10^{10}$	71.2	—
17d	$H+HO_2\rightleftarrows H_2O+O$	54	$6\cdot10^{8}$	0	[29]	$5{,}28\cdot10^{8}$	54.4	—
8	$OH+H_2O_2\rightleftarrows HO_2+H_2O$	31	$7.8\cdot10^{9}$	1.6	[31]	$8.45\cdot10^{9}$	32.6	—
14	$H+H_2O_2\rightleftarrows H_2O+OH$	66	$7.05\cdot10^{9}$	4.2	[32]	$6.4\cdot10^{8}$	72.6	—
28	$OH+OH+M\rightleftarrows H_2O_2+M$	50	$1.61\cdot10^{8}$	—9.6	—	$4.07\cdot10^{13}$	42	[33]
30	$O+H_2O_2\rightleftarrows O_2+H_2O$	42,5	$2.8\cdot10^{10}$	6.4	[32]	$4.77\cdot10^{10}$	91.4	—
14a	$H+H_2O_2\rightleftarrows H_2+HO_2$	16	$7\cdot10^{9}$	4.2	[32]	$1.6\cdot10^{9}$	20	—
29a	$HO_2+HO_2\rightleftarrows H_2O_2+O_2$	40	$2.4\cdot10^{10}$	1.5	[32]	$3.67\cdot10^{11}$	41.8	—
32	$O+H_2O_2\rightleftarrows HO_2+OH$	14	$2.8\cdot10^{10}$	6.4	[32]	$2.89\cdot10^{9}$	20.4	—
21	$CO+OH\rightleftarrows CO_2+H$	26	$2.9\cdot10^{9}$	5.7	[34]	$1.12\cdot10^{13}$	30.4	—
24	$CO+HO_2\rightleftarrows CO_2+OH$	62	$1.33\cdot10^{11}$	23	[35]	$4.26\cdot10^{12}$	85	—
43	$H_2CO+OH\rightleftarrows HCO+H_2O$	45	$3.6\cdot10^{11}$	1.5	[36]	$1\cdot10^{11}$	46.4	—
44	$H_2CO+H\rightleftarrows HCO+H_2$	30	$6\cdot10^{10}$	1.5	[37]	$3.7\cdot10^{9}$	31	—
45	$H_2CO+O\rightleftarrows HCO+OH$	28	$8.4\cdot10^{11}$	5.5	[38]	$2.3\cdot10^{10}$	33.4	—
47	$HCO+HO_2\rightleftarrows H_2CO+O_2$	26	$5.35\cdot10^{8}$	5.6	—	$3\cdot10^{8}$	32	[1]
66	$H+CO+M\rightleftarrows HCO+M$	30	$1\cdot10^{8}$	—17	—	$1.6\cdot10^{11}$	14.7	[39]
48	$H_2CO+HO_2\rightleftarrows H_2O_2+HCO$	14	$6\cdot10^{8}$	8	[1]	$1.6\cdot10^{8}$	22	—
70	$HCO+O_2\rightleftarrows HO_2+CO$	17	$6\cdot10^{10}$	7.25	[37]	$5.5\cdot10^{10}$	24.4	—
86	$HCO+O\rightleftarrows CO_2+H$	96	$1{,}2\cdot10^{9}$	0	[40]	$6.8\cdot10^{11}$	96	—
46a	$HCO+H+M\rightleftarrows H_2CO+M$	73	$6.3\cdot10^{8}$	—3.2	—	$5\cdot10^{13}$	72	[39]
68	$HCO+OH\rightleftarrows CO+H_2O$	88	$6\cdot10^{10}$	0	[37]	$8.9\cdot10^{11}$	88	—
69	$HCO+H\rightleftarrows CO+H_2$	73	$6\cdot10^{10}$	5	[37]	$1.9\cdot10^{11}$	78	—
70a	$HCO+O\rightleftarrows CO+OH$	71	$6\cdot10^{8}$	0	[41]	$8.5\cdot10^{8}$	71.6	—
31	$CH_4+OH\rightleftarrows CH_3+H_2O$	17	$6\cdot10^{10}$	8.5	[42]	$6.9\cdot10^{9}$	24.8	—
33	$CH_4+H\rightleftarrows CH_3+H_2$	2	$2\cdot10^{11}$	11.6	[43]	$4.8\cdot10^{9}$	12.5	—
35	$CH_4+O\rightleftarrows CH_3+OH$	0	$2{,}05\cdot10^{10}$	7.8	[44]	$2.2\cdot10^{8}$	7.0	—
39	$CH_4+O\rightleftarrows CH_2+H_2O$	34	$2\cdot10^{10}$	7.8	[44]	$8.3\cdot10^{8}$	41.4	—
40	$CH_3+HO_2\rightleftarrows CH_4+O_2$	54	$4.3\cdot10^{8}$	—0.4	—	$6\cdot10^{10}$	55	[1]
55	$CH_3+H+M\rightleftarrows CH_4+M$	101	$1\cdot10^{9}$	—15.8	—	$2\cdot10^{14}$	88	[45]
38	$CH_3+H_2O_2\rightleftarrows CH_4+HO_2$	14	$6.5\cdot10^{7}$	4.3	—	$6.06\cdot10^{8}$	19	[46]
42	$CH_3+CH_3\rightleftarrows CH_4+CH_2$	17	$6\cdot10^{7}$	9.24	[30]	$1.9\cdot10^{9}$	27.4	—
50	$CH_3+H_2CO\rightleftarrows CH_4+HCO$	28	$6\cdot10^{10}$	4.5	[37]	$1.5\cdot10^{11}$	33.2	—
72	$CH_3+HCO\rightleftarrows CH_4+CO$	71	$6\cdot10^{10}$	0	[37]	$7.8\cdot10^{12}$	72.2	—
53	$CH_2+H_2CO\rightleftarrows CH_4+CO$	82	$6\cdot10^{10}$	0	[37]	$6\cdot10^{11}$	82.6	—
54	$CH_3+OH\rightleftarrows CH_2+H_2O$	34	$6\cdot10^{9}$	2.76	[30]	$2.2\cdot10^{10}$	37.2	—
59	$CH_2+O\rightleftarrows HCO+H$	79	$6\cdot10^{9}$	0	[30]	$9.5\cdot10^{9}$	78.6	—
65	$CH_2+H_2O\rightleftarrows H_2CO+H_2$	39	$6\cdot10^{9}$	2.5	[30]	$7.4\cdot10^{10}$	38.2	—
57	$CH_3+O_2\rightleftarrows H_2CO+OH$	51	$3\cdot10^{10}$	10	[47]	$3.3\cdot10^{10}$	61.6	—
56	$CH_3+O\rightleftarrows H_2CO+H$	68	$1.86\cdot10^{10}$	0	[48]	$3.8\cdot10^{11}$	68.2	—
74	$CHO+H_2CO\rightleftarrows CH_3+CO_2$	28	$6\cdot10^{9}$	4.5	[30]	$1.7\cdot10^{11}$	32.2	—
5d	$CH_2+O_2\rightleftarrows CO+OH+H$	32	$6\cdot10^{9}$	3.5	[49]	$3.3\cdot10^{5}$	33.8	—
4d	$CH_2+O_2\rightleftarrows CO_2+H+H$	57	$1.8\cdot10^{8}$	0	[49]	$4\cdot10^{6}$	54.8	—
87**	$CH_3+O_2+M\rightleftarrows CH_3O_2+M$	22	$3{,}6\cdot10^{8}$	2	—	$2.73\cdot10^{15}/T$	30.6	—
88**	$CH_3O_2\rightleftarrows H_2CO+OH$	29	$1\cdot10^{12}$	25	—	$6\cdot10^{9}$	56	—
89**	$CH_3O_2+CH_4\rightleftarrows CH_3O_2H+CH_3$	13	$6\cdot10^{9}$	10	—	$6\cdot10^{9}$	23	—
90**	$CH_3O+OH\rightleftarrows CH_3O_2H$	43	$6\cdot10^{7}$	0	—	$1\cdot10^{9}$	43	—
91**	$CH_3+HO_2\rightleftarrows H_2CO+H_2O$	122	$1{,}2\cdot10^{9}$	0	—	$1{,}2\cdot10^{9}$	122	—
95	$CH+H_2O\rightleftarrows CH_2+OH$	8	$3{,}1\cdot10^{8}$	8.9	—	$6\cdot10^{9}$	18.3	[50]
96	$CH+H_2\rightleftarrows CH_2+H$	23	$6.6\cdot10^{8}$	5.1	—	$6\cdot10^{9}$	29.5	[50]
97	$CH+OH\rightleftarrows CH_2+O$	25	$3\cdot10^{9}$	4.6	—	$6\cdot10^{9}$	31	[50]
98	$CH+OH\rightleftarrows CO+H_2$	177	$6\cdot10^{9}$	0	[50]	$6{,}2\cdot10^{11}$	179	—
99	$CH+O\rightleftarrows CO+H$	175	$6\cdot10^{9}$	0	[50]	$2.8\cdot10^{11}$	177	—
1a	$CH_3OH+O\rightleftarrows CH_2OH+OH$	0	$4{,}3\cdot10^{9}$	2	[51]	$3.2\cdot10^{8}$	1	—
2a	$CH_3OH+OH\rightleftarrows CH_2OH+H_2O$	17	$6\cdot10^{9}$	7.25	[51]	$4.7\cdot10^{9}$	23.2	—
3a	$CH_3OH+H\rightleftarrows CH_2OH+H_2$	2	$1{,}3\cdot10^{9}$	8.5	[52]	$2.05\cdot10^{8}$	9.3	—
4a	$CH_3O+HO_2\rightleftarrows CH_3OH+O_2$	54	$2{,}64\cdot10^{8}$	52	[51]	$6\cdot10^{9}$	52	—
5a	$CH_3+OH+M\rightleftarrows CH_3OH+M$	92	$3.6\cdot10^{9}$	0	—	$2\cdot10^{14}$	69	[53]
6a	$CH_3O+O\rightleftarrows H_2CO+OH$	79	$6\cdot10^{9}$	0	[51]	$7.9\cdot10^{8}$	79	—
7a	$CH_3O+OH\rightleftarrows H_2CO+H_2O$	96	$6\cdot10^{9}$	0	[51]	$8.3\cdot10^{9}$	96	—
8a	$CH_3O+H\rightleftarrows H_2CO+H_2$	81	$6\cdot10^{10}$	0	[51]	$1.8\cdot10^{10}$	81	—
9a	$CH_3O+O_2\rightleftarrows H_2CO+HO_2$	25	$6\cdot10^{9}$	5.3	[51]	$2.8\cdot10^{8}$	30.5	—
1.16	$H_2CO+H+M\rightleftarrows CH_3O+M$	22	$1{,}2\cdot10^{8}T$	6.4	—	$2\cdot10^{12}$	30	[51]
1d	$C_2H_2+O\rightleftarrows CO+CH_2$	73	$2\cdot10^{10}$	3.2	[54]	$5.2\cdot10^{9}$	78	—
2d	$C_2H_2+OH\rightleftarrows CO+CH_3$	56	$7.8\cdot10^{9}$	4.64	[55]	$3.3\cdot10^{10}$	62	—
6e	$C_2H+H+M\rightleftarrows C_2H_2+M$	128	—	—	—	$6\cdot10^{9}$	96	[56]
7e	$C_2H+H_2\rightleftarrows C_2H_2+H$	25	—	—	—	$6\cdot10^{9}$	20	[56]
8e	$C_2H+O_2\rightleftarrows CO+HCO$	214	$6\cdot10^{9}$	0	[56]	—	—	—
3d	$C_2H_2+O_2\rightleftarrows CH_2+CO_2$	81	$6\cdot10^{10}$	40	—	$3{,}4\cdot10^{11}$	122	—
1b	$C_2H_4+O\rightleftarrows CH_3+HCO$	43	$6\cdot10^{9}$	0.7	[57]	$5\cdot10^{7}$	46	—
2b	$C_2H_4+OH\rightleftarrows CH_3+H_2CO$	15	$4.5\cdot10^{9}$	0.9	[58]	$1.4\cdot10^{9}$	17.4	—
3b	$C_2H_3+H_2\rightleftarrows C_2H_4+H$	1	$5.8\cdot10^{8}$	12.8	—	$6\cdot10^{9}$	12	[57]
4b	$C_2H_3+HO_2\rightleftarrows C_2H_4+O_2$	57	$1.4\cdot10^{8}$	—0.2	—	$6\cdot10^{9}$	54	[57]
5b	$C_2H_2+H_2\rightleftarrows C_2H_4$	41	$2.9\cdot10^{4}$	0	—	$1.7\cdot10^{12}/T$	42	[59]
6b	$C_2H_3+O\rightleftarrows CH_3+CO$	117	$6\cdot10^{9}$	0	[57]	$2.1\cdot10^{9}$	116	—
7b	$C_2H_3+OH\rightleftarrows CH_3+HCO$	46	$6\cdot10^{9}$	0	[57]	$1.5\cdot10^{9}$	46	—
8b	$C_2H_3+H\rightleftarrows C_2H_2+H_2$	63	$6\cdot10^{9}$	0	[57]	$6.3\cdot10^{9}$	62	—
9b	$C_2H_3+O_2\rightleftarrows C_2H_2+HO_2$	7	$6\cdot10^{9}$	10	[57]	$1.8\cdot10^{9}$	15	—
30c	$C_2H_3+OH\rightleftarrows C_2H_2+H_2O$	78	$6\cdot10^{9}$	0	[64]	$2.3\cdot10^{10}$	76	—
31c	$C_2H_3+O\rightleftarrows C_2H_2+OH$	61	$6\cdot10^{9}$	0	[64]	$2.8\cdot10^{9}$	60	—
2e	$CH_3+CH_3\rightleftarrows C_2H_4+H_2$	55	$2\cdot10^{13}$	38	[60]	—	—	—
3e	$C_2H_4+H+H\rightleftarrows CH_3+CH_3$	48	—	—	—	$6\cdot10^{10}$	41,6	[60]
2c	$CH_3+CH_3\rightleftarrows C_2H_6$	83	$8.4\cdot10^{9}$	0	[61]	$1\cdot10^{13}$	83	—
3c	$C_2H_6+OH\rightleftarrows C_2H_5+H_2O$	20	$1.8\cdot10^{11}$	4	[62]	$1.6\cdot10^{11}$	24	—
4c	$C_2H_6+H\rightleftarrows C_2H_5+H_2$	5	$7.4\cdot10^{10}$	9.6	[63]	$1.4\cdot10^{10}$	14.2	—
5c	$C_2H_6+O\rightleftarrows C_2H_5+OH$	3	$4.6\cdot10^{9}$	4	[64]	$3.8\cdot10^{8}$	7.0	—
6c	$C_2H_5+HO_2\rightleftarrows C_2H_6+O_2$	51	$3.2\cdot10^{8}$	—1.2	—	$6{,}9\cdot10^{9}$	50	[64]
7c	$C_2H_5+H_2O_2\rightleftarrows C_2H_6+HO_2$	11	$4.9\cdot10^{8}$	8	—	$6\cdot10^{8}$	19	[64]

Table 1 (cont'd.).

No. of reaction	Reaction	h, kcal mol^{-1}	Forward reaction: A, mol litre^{-1}s^{-1}	Forward reaction: E, kcal mol^{-1}	Forward reaction: Refs.	Reverse reaction: A, mol litre^{-1}s^{-1}	Reverse reaction: E, kcal mol^{-1}	Reverse reaction: Refs.
8c	$C_2H_5+OH\rightleftarrows CH_3O+CH_3$	4	$3\cdot10^{10}$	0	[64]	$8\cdot10^{9}$	1.4	—
9c	$C_2H_5+H\rightleftarrows CH_3+CH_3$	15	$4\cdot10^{10}$	0	[65]	$6,7\cdot10^{7}$	12.6	—
10c	$C_2H_5+H\rightleftarrows CH_4+CH_2$	32	$6\cdot10^{9}$	6	[64]	$3,3\cdot10^{8}$	36	—
11c	$C_2H_5+O\rightleftarrows CH_3+H_2CO$	83	$6\cdot10^{9}$	0	[64]	$2,1\cdot10^{8}$	80	—
12c	$C_2H_5+O_2\rightleftarrows CH_3O+H_2CO$	55	$6\cdot10^{8}$	10	[64]	$1,7\cdot10^{8}$	62	—
13c	$C_2H_5+O_2\rightleftarrows CH_3CHO+OH$	61	$6\cdot10^{9}$	10	[64]	$3,2\cdot10^{8}$	72	—
14c	$CH_3CHO+OH\rightleftarrows CH_3CO+H_2O$	23	$3,4\cdot10^{10}$	4	[66]	$3\cdot10^{10}$	28	—
15c	$CH_3CHO+H\rightleftarrows CH_3CO+H_2$	8	$6\cdot10^{9}$	3.4	[66]	$1.1\cdot10^{9}$	12.2	—
16c	$CH_3CHO+O\rightleftarrows CH_3CO+OH$	6	$1,1\cdot10^{10}$	2.3	[67]	$9,1\cdot10^{8}$	9.4	—
17c	$CH_3+CO_2+OH\rightleftarrows CH_3CHO+O_2$	11	$7,4\,T$	26.8	[64]	$6\cdot10^{8}$	20	—
18c	$CH_3CO+HO_2\rightleftarrows CH_3CHO+O_2$	48	$1.6\cdot10^{7}$	−17,2	—	$3\cdot10^{8}$	30	[64]
19c	$CH_3CO+H_2O_2\rightleftarrows CH_3CHO+HO_2$	8	$4,9\cdot10^{8}$	−0.8	[64]	$6\cdot10^{8}$	6	—
20c	$CH_3+HCO+M\rightleftarrows CH_3CHO+M$	68	$7.9\cdot10^{4}\,T$	−20	—	$2\cdot10^{14}$	52	[64]
21c	$CH_3+CO\rightleftarrows CH_3CO$	3	$1,5\cdot10^{2}\,T$	6.8	—	$2\cdot10^{10}$	16	[68]
22c	$CH_3CO+H\rightleftarrows CH_3+CHO$	27	$6\cdot10^{9}$	4.80	[64]	$6,6\cdot10^{7}$	28	—
23c	$CH_3CO+O\rightleftarrows CH_3O+CO$	87	$6\cdot10^{9}$	0	[64]	$1,6\cdot10^{10}$	84	—
24c	$C_2H_5+OH\rightleftarrows C_2H_4+H_2O$	85	$6\cdot10^{9}$	0	[64]	$7,2\cdot10^{8}$	80	—
25c	$C_2H_5+H\rightleftarrows C_2H_4+H_2$	70	$6\cdot10^{9}$	0	[64]	$1,6\cdot10^{9}$	66	—
26c	$C_2H_5+O\rightleftarrows C_2H_4+OH$	68	$6\cdot10^{9}$	0	[64]	$6.9\cdot10^{8}$	64	—
27c	$C_2H_4+H+M\rightleftarrows C_2H_5+M$	33	$3\cdot10^{2}\,T$	2	—	$6\cdot10^{9}$	40	[64]
28c	$C_2H_5+O_2\rightleftarrows C_2H_4+HO_2$	14	$6,9\cdot10^{9}$	8	[64]	$4,5\cdot10^{8}$	18	—
1e	$C_2H_5+H_2\rightleftarrows CH_3+CH_4$	12	$8.7\cdot10^{10}$	9	—	$6.9\cdot10^{9}$	21	[56]
4e	$C_2H_5+H\rightleftarrows C_2H_6$	98	—	—	—	$1\cdot10^{13}$	98	[56]
2.1	$CH_3NH_2+O\rightleftarrows CH_3NH+OH$	15	$1,45\cdot10^{10}$	2.57	[69]	$2,4\cdot10^{9}$	17,5	—
2.2	$CH_3NH_2+OH\rightleftarrows CH_3NH+H_2O$	32	$6,1\cdot10^{9}$	0.45	[70]	$9,5\cdot10^{9}$	32	—
2.3	$CH_3NH_2+H\rightleftarrows CH_3NH+H_2$	17	$6,3\cdot10^{10}$	5.3	[71]	$2.1\cdot10^{10}$	22	—
2.4	$CH_3+NH_2\rightleftarrows CH_3NH_2$	81	$5,8\cdot10^{6}\,T$	9.4	—	$1\cdot10^{16}$	84,4	[72]
2.5	$CH_3NH+HO_2\rightleftarrows CH_3NH_2+O_2$	30	$5,5\cdot10^{8}$	−0,35	—	$6\cdot10^{9}$	39	[69]
2.6	$CH_3NH+O\rightleftarrows CH_3O+NH$	14	$6\cdot10^{10}$	0	[69]	$1,5\cdot10^{9}$	14	—
2.7	$CH_3NH+OH\rightleftarrows CH_4+HNO$	40	$6\cdot10^{9}$	0	[69]	$3.2\cdot10^{9}$	40	—
2.8	$CH_3NH+H\rightleftarrows CH_3+NH_2$	15	$6\cdot10^{10}$	0	[69]	$5.3\cdot10^{7}$	14	—
2.9	$CH_3NH+O_2\rightleftarrows CH_3O+HNO$	12	$6\cdot10^{9}$	4	[69]	$3.1\cdot10^{8}$	15	—
2.10	$NH_2+H+M\rightleftarrows NH_3+M$	104	$3,2\cdot10^{8}\,T$	−15	—	$1,2\cdot10^{13}$	91	[73]
2.11	$NH_2+HO_2\rightleftarrows NH_3+O_2$	56,5	$2,5\cdot10^{8}$	−1.4	—	$6.9\cdot10^{9}$	56	[69]
2.12	$NH_2+OH\rightleftarrows NH_3+O$	2,5	$5,7\cdot10^{7}$	1.6	—	$1\cdot10^{9}$	4.8	[74]
2.13	$NH_2+O\rightleftarrows HNO+H$	25	$6\cdot10^{8}$	0	[69]	$3,8\cdot10^{9}$	25	—
2.14	$NH_2+NO\rightleftarrows N_2+H_2O$	120	$1.1\cdot10^{9}$	0	[75]	$1.4\cdot10^{10}$	122	—
2.15	$NH_2+NH_2\rightleftarrows NH_3+NH$	15	$6\cdot10^{10}$	10	[69]	$4,3\cdot10^{11}$	25	—
2.16	$NH_2+NH\rightleftarrows NH_3+N$	21	$6\cdot10^{10}$	4	[69]	$2,8\cdot10^{12}$	26	—
2.17	$NH_3+OH\rightleftarrows NH_2+H_2O$	14.5	$3.2\cdot10^{9}$	1.84	[76]	$2\cdot10^{9}$	15.6	—
2.18	$NH_3+H\rightleftarrows NH_2+H_2$	0	$2.7\cdot10^{10}$	17,4	[73]	$3,6\cdot10^{9}$	15.2	—
2.19	$HNO+OH\rightleftarrows NO+H_2O$	69	$6\cdot10^{8}$	0	[69]	$1.3\cdot10^{9}$	70	—
2.20	$NH+NO\rightleftarrows N_2+OH$	93	$1\cdot10^{9}$	0	[77]	$6.6\cdot10^{9}$	94	—
2.21	$HNO+O\rightleftarrows NO+OH$	52	$6\cdot10^{9}$	0	[78]	$1.3\cdot10^{9}$	53	—
2.22	$NH+O_2\rightleftarrows NO+OH$	50	$5,1\cdot10^{9}$	0	[79]	$3,1\cdot10^{6}$	50	—
2.23	$NH+OH\rightleftarrows NO+H_2$	69	$1,6\cdot10^{8}\,T^{0.50}$	1.5	[55]	$2.5\cdot10^{9}\,T^{0.50}$	70	—
2.24	$NH+H\rightleftarrows N+H_2$	20	$6\cdot10^{10}$	4,2	[69]	$2.5\cdot10^{11}$	25	—
2.25	$NH+O\rightleftarrows N+OH$	18	$6\cdot10^{10}$	5	[69]	$1,1\cdot10^{11}$	24	—
2.26	$HNO+H\rightleftarrows NO+H_2$	55	$6\cdot10^{10}$	0	[69]	$2,8\cdot10^{10}$–	55	—
2.27	$NH+NH\rightleftarrows NH_2+N$	6.8	$6\cdot10^{10}$	8	[69]	$3.9\cdot10^{11}$	15	—
2.28	$CH_2+NH\rightleftarrows HN+H_2$	117	$6\cdot10^{10}$	0	[69]	$1,5\cdot10^{12}$	116	—
2.29	$CH_2+N\rightleftarrows HCN+H_2$	118	$6\cdot10^{10}$	0	[80]	$2.9\cdot10^{11}$	115	—
2.30	$CH+NH_2\rightleftarrows HCN+H_2$	153	$6\cdot10^{9}$	0	[69]	$5.7\cdot10^{11}$	154	—
2.31	$CN+H+M\rightleftarrows HCN+M$	122	$1.83\cdot10^{8}\,T$	−9.4	—	$5.8\cdot10^{13}$	117	[81]
2.32	$CN+H_2O\rightleftarrows HCN+OH$	4	$5.1\cdot10^{9}$	4.1	[69]	$6\cdot10^{9}$	10.5	—
2.33	$CN+H_2\rightleftarrows HCN+H$	19	$6\cdot10^{10}$	5.3	[82]	$3.6\cdot10^{11}$	27	—
2.34	$CN+OH\rightleftarrows HCN+O$	21	$1,32\cdot10^{-1}\,T^{2.286}$	−18.2	—	$1.79\,T^{2.286}$	5.2	[83]
2.35	$CN+O_2\rightleftarrows CO+NO$	106	$6\cdot10^{9}$	0	[69]	$6,8\cdot10^{9}$	110	—
2.36	$CN+OH\rightleftarrows CO+NH$	57	$6\cdot10^{9}$	0	[69]	$1.6\cdot10^{10}$	60	—
2.37	$CN+O\rightleftarrows CO+N$	74	$6\cdot10^{9}$	0	[69]	$3\cdot10^{10}$	78	—
2.38	$CN+NO\rightleftarrows CO+N_2$	149	$7.2\cdot10^{7}$	0	[84]	$1.3\cdot10^{9}$	154	—
2.39	$CN+NH_3\rightleftarrows HCN+NH_2$	18.5	$6\cdot10^{9}$	6.9	[85]	$4.8\cdot10^{9}$	27	—
2.40	$HCN+OH\rightleftarrows NH_2+CO$	24	$6\cdot10^{8}$	6	[69]	$4.2\cdot10^{9}$	31	—
2.41	$HCN+NH\rightleftarrows CH_2+N_2$	30	$6.8\cdot10^{8}$	0	—	$2,8\cdot10^{9}$	30	[86]
2.42	$N+HCN\rightleftarrows CH+N_2$	2	$7.2\cdot10^{9}$	9.3	[87]	$8\cdot10^{8}$	11	—
1.3	$NO+HO_2\rightleftarrows NO_2+OH$	8	$8.7\cdot10^{8}$	0	—	$6\cdot10^{9}$	8	[88]
1.4	$NO_2+H\rightleftarrows NO+OH$	29	$2.9\cdot10^{10}$	0	[88]	$3.5\cdot10^{8}$	29.4	—
1.5	$NO+O+M\rightleftarrows NO_2+M$	72	$5.8\cdot10^{4}\,T$	−8.6	—	$1.1\cdot10^{13}$	65	[89]
1.6	$NO_2+O\rightleftarrows NO+O_2$	46	$1\cdot10^{10}$	0.6	[89]	$2.2\cdot10^{9}$	46	—
1.7	$NO+NO+O_2\rightleftarrows NO_2+NO_2$	26	$4.9\,T$	−0.6	—	$4\cdot10^{9}$	27	[89]
1.8	$NO+NO_3\rightleftarrows NO_2+NO_2$	23	$1.5\cdot10^{7}$	1.3	—	$7.8\cdot10^{8}$	24	[89]
1.9	$NO_2+O+M\rightleftarrows NO_3+M$	49	$2.8\cdot10^{7}\,T$	−7.8	—	$1\cdot10^{14}$	43	[89]
1.10	$NO+O_2+M\rightleftarrows NO_3+M$	3	$7.65\,T$	−1.7	—	$1,2\cdot10^{8}$	3.2	[89]
1.11	$CH_3+NO_2\rightleftarrows CH_3O+NO$	18	$1.3\cdot10^{10}$	0	[90]	$2.46\cdot10^{10}$	18	—
1.12	$N+NO\rightleftarrows N_2+O$	75	$2.75\cdot10^{10}$	0.5	—	$5\cdot10^{10}$	75	[91]
1.13	$N+O_2\rightleftarrows NO+O$	32	$1\cdot10^{10}$	7.5	[55]	$2\cdot10^{9}$	39.4	—
1.14	$NO+NO\rightleftarrows N_2+O_2$	43	$1.41\cdot10^{12}$	85	[91]	$2.85\cdot10^{13}$	128	—
1.15	$N+OH\rightleftarrows NO+H$	49	$4\cdot10^{10}$	0	[92]	$1,5\cdot10^{11}$	48.6	—
1.1	$NO_2+OH+M\rightleftarrows HNO_3+M$	48	—	—	—	$6\cdot10^{11}$	30.1	[88]
1.2	$OH+HNO_3\rightleftarrows NO_3+H_2O$	18	$5,4\cdot10^{7}$	0	[93]	—	—	—

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*The reactions are grouped in terms of substances; the numbering used in the original papers has been retained.

**The combination of the Arrhenius parameters of these processes selected for the description of cold flames.[94]

The mechanisms indicated above describe satisfactorily the course of the reaction in an atomic-oxygen hydrogen flame when oxygen atoms and molecular hydrogen are rapidly mixed in the stream.[95] An important part of the scheme, particularly at pressures close to and above the second limit, are reactions involving hydrogen peroxide.[96] The latter is formed during the oxidation of H_2 as an intermediate and the allowance for such reactions makes it possible to achieve a satisfactory agreement between the calculated and experimental second ignition limits.[96]

A fairly universal DKM, describing the hydrogen oxidation and combustion reaction over a wide range of temperatures, pressures, and mixture compositions, should apparently contain a greater number of elementary steps than in the calculations quoted above. It should consist of at least three parts including (a) chain initiation, propagation, branching, and linear termination processes when the rate of termination is proportional to the concentration of the active centre (with a power exponent of unity under all conditions), (b) quadratic termination processes the rate of which is proportional to the square of the concentration of the active centre, i.e. recombination reactions (at high concentrations of the active species at high temperatures and for high degrees of combustion), and (c) reactions involving hydrogen peroxide, which make a large contribution at high pressures.

A fairly detailed mechanism, incorporating more than 20 processes satisfying the above requirements, has been described in a number of communications[2,97–99] (the first 22 forward and reverse processes in Table 1). The validity of this DKM has been tested by a series of calculations modelling the self-ignition and combustion in the spreading flame.

In self-ignition, the initial reaction stage is not outwardly manifested in any way and a sharp increase in the rate of reaction and evolution of heat, passing into explosion, are observed only after a certain time, called the self-ignition delay, has elapsed. Calculation of the self-ignition delay time makes it possible to follow the initial stages of the reaction, where the concentration of the initial reactants hardly changes.

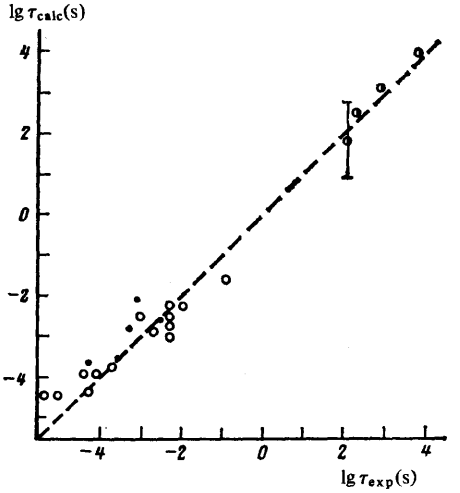

Figure 2. Comparison of the calculated[30,46,97,98] and experimental self-ignition delays; $[H_2]_0$ = 1–8%, $[CH_4]_0$ = 2–33%, $[O_2]_0$ = 1–67%, T = 696–2130 K, P = 0.167–5 atm (according to the data in Refs.100–112).

An example of a comparison of hydrogen ignition delays, measured and calculated on the basis of the DKM on the assumption that a purely branched chain process takes place, is given in Fig.2 (filled symbols). The delays were calculated with the aid of a standard program by solving a system of material balance equations (I). A sharp increase in the rate of the chemical reaction, indicating the occurrence of self-ignition, was adopted as a criterion at the end of the delay. The experimental data refer to the temperature range 979–2130 K and the pressure range 0.23–5 atm. Evidently the discrepancy between the measured and calculated delay does not exceed one order of magnitude.

We shall now proceed to the examination of reactions in a mixture containing hydrogen peroxide as the initial reactant. Since hydrogen peroxide occurs in the DKM (Table 1), the latter can be used without any changes. The mechanisms of the reactions of H_2O_2 have been investigated in a number of studies. Thus the rate constant for reaction (−28) has been determined[113] for the conditions prevailing at the beginning of the thermal decomposition of H_2O_2 (Table 1). In another study[32] the investigation was carried out under flow conditions at low pressures. The authors determined the important rate constants for reactions of H_2O_2 with hydrogen and oxygen atoms. Under these constants, calculations have been performed[27] on the basis of the DKM for the conditions of the experiment adopted in previous calculations.[32,113] Thus the experimental[32] and calculated concentrations of H_2, H, O, O_2, H_2O, and H_2O_2 in the reaction of H_2O_2 with O (453 K, 0.124 atm) were compared; a comparison was also made of the experimental[113] and calculated $[H_2O_2]$ and $[HO_2]/[H_2O_2]_0$ in the H_2O_2 decomposition reaction (1060 K, 6.2 atm) as a function of the reaction time and of the yield of H_2O_2 as a function of its initial concentration in the reaction of the peroxide with the products of a discharge in a hydrogen–oxygen mixture containing hydrogen atoms $\{[H]_0$ = 0.04%$\}$ and hydroxy-radicals $\{[OH]_0$ = 0.0114%$\}$ at 803 K, a pressure of 0.01 atm, and for a reaction time of 1.7 ms. It was found that the calculations permit a qualitatively correct description of the course of the reaction of H_2O_2 in the temperature range 453–1060 K and in the pressure range 0.01 to 6.2 atm.

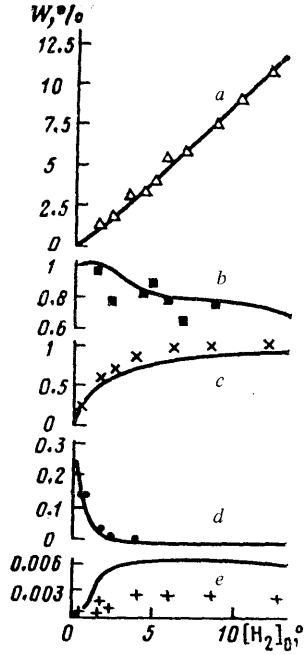

Figure 3. Dependence of the yield of the reaction products on the initial H_2 concentration for the oxygen atomic flame with hydrogen;[28] $[O]_0$ = 0.5%, $[O_2]_0$ = 0.82%, T = 1169 K, P = 0.01 atm, t = 2.5 ms: symbols—experiment; lines—calculation; a) H_2; b) O_2; c) H; d) O; e) OH.

It has been shown[27] that failure to take into account the reactions of hydrogen peroxide at 803–1038 K near the ignition peninsula in the combustion of hydrogen–oxygen mixtures can lead to appreciable errors, but at temperatures above 1200 K these reactions can be disregarded.

As the kinetics and rate constants for different stages are refined, it becomes possible to obtain a more accurate and reliable description of the hydrogen combustion process. This can be seen from the comparison of the calculated and experimental yields of the products obtained for the atomic-oxygen hydrogen flame[28] (Fig.3).

The results of numerous studies on the mechanism of the combustion of hydrogen are also presented in a review,[114] in a monograph,[115] a number of communications,[116–118] etc. They consider the mechanisms involving virtually the same reactions as those listed in Table 1. Thus one may note the unity of the views of different investigators concerning the principal processes in the DKM of the oxidation of hydrogen. We may also note that algorithms have been proposed in a number of studies, for example in Refs.115 and 116, for the identification of the reactions important under the specific conditions considered and for the construction of abbreviated kinetic schemes.

III. C_1–C_2 HYDROCARBONS AND METHANOL

1. The Combustion of Methane

The experience gained in the study of the mechanism of the combustion of hydrogen has shown that the chemical reaction can be described with a satisfactory accuracy under most varied conditions. The next step as regards complexity involves the construction of the DKM for the oxidation and combustion of methane (including the combustion of carbon monoxide and formaldehyde appearing as intermediates).

Extensive experimental data on the kinetics of the oxidation of methane, referring mainly to the region of low temperatures (below 900 K), have been examined in monographs and communications.[1,6,12,13,111,112,119,120]

On the basis of data for the low-temperature oxidation and high-temperature processes in flames, a number of workers[43,48,121–123] demonstrated that reactions involving the active centres of the hydrogen–oxygen flame (OH, H, and O) and molecular hydrogen play an important role in the conversion of methane. Thus, according to Westenberg and Fristrom,[121] the methane oxidation reaction# in the flame proceeds as follows:

$$CH_4+OH\rightarrow CH_3+H_2O, \qquad (31)$$

$$CH_4+O\rightarrow CH_3+OH, \qquad (35)$$

$$CH_3+O_2\rightarrow H_2CO+OH, \qquad (57)$$

$$H_2CO+OH\rightarrow HCO+H_2O. \qquad (43)$$

$$HCO+OH\rightarrow CO+H_2O, \qquad (68)$$

$$CO+OH\rightarrow CO_2+H, \qquad (21)$$

$$H+H_2O\rightarrow OH+H_2, \qquad (-1)$$

$$O+H_2\rightarrow OH+H, \qquad (-6)$$

$$OH+OH\rightarrow H_2O+O, \qquad (9)$$

$$H+O_2\rightarrow OH+O, \qquad (-4)$$

$$O+O+M\rightarrow O_2+M. \qquad (12)$$

The basis of the mechanism formulated here is the reactions of the active centres O and OH with the initial methane and the reactions ensuring the degenerate chain branching by hydrogen. The principal direction of the transformation corresponds to the sequence

$$CH_4\rightarrow CH_3\rightarrow H_2CO\rightarrow HCO\rightarrow CO\rightarrow CO_2.$$

Molecular hydrogen and water also appear during the reaction.

Quantitative calculations, carried out approximately within the framework of the mechanism described above, enabled a number of workers[124–126] to describe satisfactorily the experi-experimental data.

In a number of studies[30,97–99] an attempt was made also simultaneously to elucidate to what extent the reaction scheme based on a mechanism similar to that described above but including a greater number of possible elementary steps with participation of species involved in the scheme proposed by Westenberg and Fristrom[121] may be universal. It is essential to elucidate also the contributions of these new reactions to the DKM and to determine whether their introduction is really necessary. The scheme under test is wholly based on the DKM of the oxidation of hydrogen and numerous probable but as yet uninvestigated reactions of the radicals generated during the combustion of methane (CH_3, CH_2, CH, and HCO) have been introduced. The possible elementary steps were selected taking into account their probable rates on the basis of the following rules: all reactions (apart from several active centre initiation reactions) with a high activation energy were excluded; also excluded were almost all the reactions accompanied by a change in multiplicity (in conformity with the Wigner rule). Analysis showed that the methane oxidation pathway leading to the final product involving the CH species is less probable than other possible pathways and this species and its reactions were not therefore included in the scheme.

Ultimately the kinetic mechanism incorporating processes ranging from (1) to (74) in Table 1 was adopted. It does not include several well known reactions. Among them in the recombination of methyl radicals with formation of ethane, which takes place in accordance with the equation

$$CH_3+CH_3\rightarrow C_2H_6. \qquad (2c)$$

Analogous processes lead to the formation of other hydrocarbons. These reactions are followed by the interactions of hydrocarbons with the active centres, etc. Allowance for all these reactions entailed a very great increase in the complexity of the mechanism. In the proposed scheme chain termination as a result of the recombination of methyl radicals is simulated by reaction (42).

The rate constants were taken from the literature sources and, when these were lacking, the activation energy was determined from semiempirical formulae:[1] for exothermic reac-reactions, $E = 11.5 - 0.25h$ for $h \leq 46$ and $E = 0$ for $h > 46$; for endothermic reactions, $E = 11.5 + 0.75h$ (h is the heat of reaction in kcal mol^{-1} [127]). The pre-exponential factor A for a bimolecular reaction is approximately 10^{-11} cm^3 $molecule^{-1}$ s^{-1} (6×10^9 litre mol^{-1} s^{-1}). The values of A and E for the reverse reactions have been calculated from the equilibrium constants given by Gurvich et al.[127] If the activation energy for the endothermic process is smaller than h for the reaction, then the activation energy for the reverse process is found to be negative. In this case an extremely high rate constant may be obtained at low temperatures. This is a consequence of the deviation of the temperature variation of the rate constant from the Arrhenius straight line and must be taken into account in the calculations at low temperatures. Naturally, the parameters of the rate constants thus obtained

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#Here and henceforth the numbers of reactions are given in accordance with Table 1.

constitute only an extremely rough and approximate estimate. The values of A and E obtained in the calculations have been corrected when necessary. Clearly, in the presence of a large number of roughly estimated parameters the correction can also be fairly approximate. The total number of elementary reactions in the initial version of the DKM reached 86 (the forward and reverse processes).[30]

The DKM obtained was tested primarily in the calculation of the arrest of the self-inflammation over a wide range of initial conditions: temperatures from 979 to 2130 K, pressures from 0.167 to 3 atm (Fig.2, open symbols). At the same time, the yields of products in the shock tube and in the atomic flame of methane were modelled. The products formed in such a flame (0.01 atm) have been analysed in greater detail by Basevich et al.[37]

Comparison of all these calculations with experiments yielded yielded more or less satisfactory results. An acceptable agreement has been obtained in the description of the propagation of the methane flame.[128] In the latter case the calculation was performed using Eqn.(III) on the assumption of a stepwise temperature rise in the combustion zone:

$$x<0,\ T=T_0\ ,$$
$$x\geqslant 0,\ T=T_c.$$

The values of T_c and the rates of propagation of the flame were specified on the basis of experimental data.[129] Account was taken only of reactions which make the greatest contribution to the process under specific conditions of the calculation.

The extension of the DKM described above to the low-temperature region did not require any fundamental changes.[46] It has been possible to calculate the reaction half-lives in satisfactory agreement with experiment up to hundreds of minutes (Fig.2, half-filled symbols). The processes significant for the DKM, whose contribution to the yield of products throughout the range of calculated conditions is either between 10 and 100% (approximately 30–40 elementary steps including certain forward and reverse reactions) or between 1 and 10% (a further approximately 30 processes) have been selected on the basis of the calculations performed. If account is taken of the possible occurrence of the above reactions in the forward and reverse directions, then one obtains 2 × 55 processes including also processes (5d) and (4d), which were added later—see below. We may note that the processes have been selected by Basevich et al.[46] by comparing the integrals of the rate of reaction over the periods covered by the calculation:

$$I=\int_{\tau} w_{ij}\,dt\,. \qquad \text{(V)}$$

Such comparison showed that methane is consumed mainly in the processes

$$CH_4+OH\rightarrow CH_3+H_2O \qquad (31)$$

and

$$CH_4+H\rightarrow CH_3+H_2. \qquad (33)$$

The main source of H atoms is the reaction

$$H_2+OH\rightarrow H_2O+H\,. \qquad (1)$$

Water is formed in the reactions

$$CH_4+OH\rightarrow CH_3+H_2O, \qquad (31)$$

$$H_2CO+OH\rightarrow HCO+H_2O, \qquad (43)$$

and

$$H_2+OH\rightarrow H_2O+H. \qquad (1)$$

Carbon monoxide is obtained in the processes

$$HCO+M\rightarrow H+CO+M \qquad (-66)$$

and

$$HCO+O_2\rightarrow CO+HO_2\ , \qquad (70)$$

while carbon dioxide is produced in the reactions

$$CO+OH\rightarrow CO_2+H, \qquad (21)$$

and

$$CO+HO_2\rightarrow CO_2+OH. \qquad (24)$$

The greatest yield of hydrogen is obtained from the process

$$CH_4+H\rightarrow CH_3+H_2\,. \qquad (33)$$

Degenerate branching takes place at the H_2O_2, H_2, and H_2CO molecules. After the selection of the leading reactions steps, it was found that at 700–1000 K the rate of branching is a maximum due to the process

$$H_2O_2+M=OH+OH+M\,, \qquad (-28)$$

while at T > 1200 K the main branching process becomes the reaction

$$H+O_2=OH+O. \qquad (-4)$$

The addition of reactions (87)–(91) and (2c) from Table 1 to the kinetic scheme for the combustion of methane proposed by Basevich et al.[46] makes it possible to model, on the basis of Eqns.(I) and (II), the reaction in the region of cold flames and the cold-flame flash[94] observed by Vanpee[130] (here it is necessary to take into account the thermal regime in the reaction). Furthermore, it is necessary to modify the Arrhenius parameters of the rate constants for stage (57) which had given rise to doubts (the new values are A = 1.56 × 10^9 litre mol^{-1} s^{-1} and E = 25 kcal mol^{-1}). Analysis of the solution showed[94] that the mechanism of the cold flame includes the initial activation of the oxidation reaction and subsequent inhibition owing to the thermal decomposition of the peroxy-radical, the formation of formaldehyde from the latter, and the interaction of formaldehyde with the leading active centres. Additional tests showed that the changes in the kinetic parameters introduced for the description of the cold flame do not affect the calculated characteristics of the reaction outside this region.

Criteria have been proposed[131] for the estimation of the accuracy of the calculations based on the DKM for the combustion of methane. Quantities characterising the deviation of the experimental parameters X_{exp} from the calculated X_{calc}, i.e.

$$pM=\lg\left(X_{calc}/X_{exp}\right)$$

have been calculated for the eight DKM for the oxidation of methane proposed in the literature. The induction period, the coefficient in the exponent defining the growth of the concentration of CO_2 during the induction period (β_{CO_2}), and the analogous coefficient for the chemiluminescence of the excited radical CH* (β_{CH^*}) and the CO molecule (β_{CO}) (Table 2) were adopted as the parameters. The values of pM obtained,[132] corresponding to the DKM for the oxidation of methane proposed by Basevich et al.[46], are presented in Table 2; the average logarithm of the deviation of the calculated quantities is 0.03 and the mean square logarithm of the deviation is 0.33 (the deviation corresponds to a coefficient of ~2). In general, these deviations are not worse than the values calculated by Olsen and Gardiner[131] especially since the experimental parameters selected by the authors[131] were in no way optimised.

Table 2. Comparison of the calculated and experimental parameters of the oxidation of methane.

Parameter X	T, K	P, atm	Composition, % (remainder-Ar)			Value of X		pM	
			CH_4	CO	O_2	experiment*	calculation (Ref.132)	from Ref.132	from Ref.131
τ, s	1750	0.28	1.67	—	3.33	$1.38\cdot10^{-3}$	$0.34\cdot10^{-3}$	−0.61	−0.72÷0.56
τ, s	2000	0.33	1.67	—	3.33	$3.2\cdot10^{-4}$	$0.7\cdot10^{-4}$	−0.66	
τ, s	2000	0.15	0.05	4.32	2.13	$3.3\cdot10^{-4}$	$2.5\cdot10^{-4}$	−0.12	−0.8÷0.08
β_{CO_2}, s^{-1}	2000	0.15	0.05	4.32	2.13	$4.6\cdot10^{3}$	$9.6\cdot10^{3}$	0.32	
β_{CH^*}, s^{-1}	1800	1.5	1	—	1	$2.6\cdot10^{5}$	$2.6\cdot10^{5}$	0	−0.3÷1.0
β_{CH^*}, s^{-1}	2400	1.9	1	—	1	$7.15\cdot10^{6}$	$7.3\cdot10^{6}$	−0.02	
[CO] [O], mol^2cm^{-6}	2195	1.43	1	2	2	$3.8\cdot10^{-15}$	$1.8\cdot10^{-16}$	−0.31	−0.3÷0.3
Δt_{max}, s	2195	1.43	1	2	2	$2.1\cdot10^{-5}$	$5\cdot10^{-5}$	0.38	
β_{CO}, s^{-1}	1600	1.14	0.21	1.06	19.5	$3.0\cdot10^{4}$	$6.1\cdot10^{4}$	0.31	−0.04÷0.6
β_{CO}, s^{-1}	1600	1.13	0.02	1.03	19.4	$1.2\cdot10^{4}$	$2.2\cdot10^{4}$	0.27	
$d[CH_3]/dt$, mol $cm^{-3}s^{-1}$	1600	10	1	—	2	$1.8\cdot10^{-5}$	$3.2\cdot10^{-5}$	0.25	0.08÷2.13
$d[CH_3]/dt$, mol $cm^{-3}s^{-1}$	1820	10	1	—	2	$3.9\cdot10^{-4}$	$3.5\cdot10^{-4}$	−0.05	
$\Delta[CH_4]_{rel}$	2200	0.25	9	—	1	0.017	0.0081	−0.32	−0.8÷0.02
$\Delta[CH_4]_{rel}$	2500	0.25	9	—	1	0.01	0.014	0.15	

Notation: τ is the induction period, Δt_{max} the time from the start of the reaction until the attainment of $\{[CO][O]\}_{max}$, and $\Delta[CH_4]_{rel}$ is the change in the relative concentration after $(0.2-2)\times10^{-4}$ s.

*According to Olson and Gardiner.[131]

A kinetic mechanism of the combustion of methane has also been described in other communications,[117,133–137] etc.

2. Combustion of Methyl Alcohol

The study of the combustion of CH_3OH is important intrinsically and also because methanol is usually formed as a side product in the combustion of methane and other hydrocarbons. A possible mechanism of the oxidation of methanol has been examined[51] in relation to its flame with atomic oxygen. We shall now turn to the kinetics of this process.

In the primary step of the interaction of oxygen atoms with methanol, the CH_2OH radical and the hydroxylradical are apparently formed.[138,139] Formaldehyde, which has also been considered[140] as a primary product, appears in our view in a subsequent elementary step involving the interaction of CH_2OH with O and H atoms, with the hydroxylradical, and molecular oxygen. Qualitatively the same picture holds also in the case where the methoxyradical is obtain instead of the alcohol radical.

There are no grounds for the belief that the subsequent course of the reactions of formaldehyde and the resulting molecular hydrogen involves any specific stages characteristic solely of the oxidation of methanol. It most probably involves the same processes by which they react as intermediates in the oxidation of methane. This has been confirmed by the study of the characteristic features of the formation of carbon monoxide, hydroxylradicals, and atomic hydrogen in the course of the O + CH_3OH reactions.

Thus, a quantitative description of the interaction of methanol with oxygen atoms requires the addition of the processes specified above of the reactions of methanol and the radical [Table 1, reactions (1a)–(9a)]. Among these reactions, at the beginning of the investigation[51] only the rate constants for reactions (1a) and (3a) were known. For the remaining seven reactions, the rate constants were adopted on the basis of semiempirical estimates. In the CH_3OH reaction mechanism these processes are then followed[51] by the reactions of formaldehyde and its formyl radical, carbon monoxide, and hydrogen. At sufficiently high temperatures, this mechanism presupposes the occurrence of a chain reaction, formaldehyde and hydrogen playing the role of intermediates ensuring degenerate branching.

On the basis of this mechanism, kinetic calculations have been made of the yields of all the analysed reaction products at a constant temperature and pressure.[51] Qualitative agreement between calculation and experiment has been observed. The maximum coefficient of deviation does not exceed 5.

The calculations performed make it possible to estimate the role of individual steps in the overall mechanism of the oxidation of CH_3OH.[51] We shall now consider the reactions of methanol and its radical. The interaction of CH_3OH with with oxygen atoms [reaction (1a)] initiates oxidation and its rate determines to a large extent also the degree of reaction. However, the reactions of CH_3OH with OH [reaction (2a)] and H [reaction (3a)], formed during the reaction, also influence the yields of all the products although to a much smaller extent. Thus an increase of the rate constant k_{2a} by an order of magnitude alters the yield of H_2CO, CO, and H by 5–9%. The increase of the rate constant k_{3a} (according to the data of Aders[141]) alters the yields of H_2CO, CO, and H_2 by 5–20%. The yields of all the products depend especially strongly on the rate constants for the reactions of CH_2OH with O, H, and OH; when these quantities are varied within the limits of one order of magnitude, the corresponding yields change from several to hundredths per cent. The reaction of CH_2OH with O_2 is less important: the analogous change in the constant alters the yields of products by less than 10%. The high activation energies for reactions (−4a) and (−5a) show that they can play a significant role only in the absence of initiation and at high temperatures. Calculations have shown that, under the given conditions, the reactions of hydrogen peroxide also influence the yields of all the products albeit only slightly.[51]

The kinetic mechanism of the combustion of methanol has likewise been considered in other studies.[137,142,143]

3. The Combustion of Acetylene

Kinetic mechanisms of the oxidation of acetylene have been proposed in a number of studies (for example in Refs.144 to 147) and the rate constants of certain elementary stages have been determined. Although these mechanisms differ, they also have much in common. According to the majority of investigators, the main reactions involving the consumption of acetylene in the combustion of weak mixtures are

$$O+C_2H_2\rightarrow CO+CH_2 \qquad (1d)$$

and

$$OH+C_2H_2\rightarrow CO+CH_3\ . \qquad (2d)$$

In addition, there is no doubt that other reactions in which acetylene is consumed also occur, in particular, the reaction of H atoms with C_2H_2. Presumably the kinetics of the subsequent reactions of the carbon monoxide and methyl and methylene radicals formed in the stages (1d) and (2d) are similar to those which obtain in the combustion of methane. This makes it possible to construct a theoretical scheme for the oxidation of acetylene–oxygen mixtures, based on the general ideas concerning the combustion of methane, which is sufficiently complete for the description of all the main reaction products.[49] However, this scheme is unsuitable for the description of the combustion of rich mixtures of acetylene and of its cracking, since this process includes heterogeneous stages which have not been investigated.

According to Basevich et al.[49], the combustion of acetylene begins with two reactions in which it is consumed [reactions (1d) and (2d)] and this is followed by branching as a result of the reactions

$$CH_2+O_2\rightarrow CO+OH+H \qquad (5d)$$

and

$$CH_2+O_2\rightarrow CO_2+2H \qquad (4d)$$

(see Table 1). The second reaction has been discussed in the literature (for example, in Refs.147 and 148). Calculations have shown[49] that the inclusion of even one of them ensures the necessary rate of propagation of the flame. The subsequent part of the mechanism corresponds to the DKM for methane [reactions (1)–(14), (14a), (17), (17a), (17d), (19), (21), (24), (26), (27), (28), (29a), (30)–(33), (35), (42)–(45), (46a), (47), (48), (54), (57), (59), (66), (68), (69), (70), (70a), (83), and (1d)–(5d) in Table 1].

This mechanism is applicable also in the region of relatively low temperatures, since the reactions of hydrogen peroxide, which play an appreciable role in the region $T < 1200$ K, are fairly completely represented here. Table 1 also indicates the Arrhenius parameters of the rate constants for reactions (1d) and (2d) taken from the literature. The rate constants for reactions (5d) and (4d) were selected by calculation. A stepwise temperature rise in the reaction zone is postulated. The calculations were performed for the conditions used in the study of Eberius et al.[147], in which the yields of the final and intermediate products generated in a planar acetylene flame were obtained. In these experiments the conditions were as follows: $[C_2H_2]_0 = 7.2\%$, $[O_2]_0 = 89.2\%$, the remainder comprising He and Ar; $P = 0.0144$ atm and $T = 960$ K. It follows from the comparison of the experimental and calculated[49] profiles that, when no account is taken of reactions (5d) and (4d), it is essential to adopt a somewhat high rate constant for the reaction

$$CO+OH\rightarrow CO_2+H\ . \qquad (21)$$

On the other hand, if one adopts an "average" rate of reaction (21) with the Arrhenius parameters $A = 2.9 \times 10^9$ litre $mol^{-1}\ s^{-1}$ and $E = 5.7$ kcal mol^{-1},[34] then it is necessary to include step (5d) or (4d) with a fairly high rate constant ($\sim 1.8 \times 10^6$ litre $mol^{-1}\ s^{-1}$). It is noteworthy that the inclusion of reaction (5d) or (4d) in the methane oxidation mechanism hardly affects the calculated rate of combustion of methane, since in this case the formation of CH_2 is a side reaction.

The calculated and experimental concentrations of the products in the reaction zone agree well with one another and one may conclude that the mechanism is reliable and that the choice of reaction rate constants is correct. One can also conclude that the mechanisms of the oxidation of acetylene and methane are similar, which permits the use of a single approach to their description.

The kinetic mechanism of the combustion of acetylene has also been described in other communications.[117,137,149,150]

4. The Combustion of Ethylene

Experiments have shown[151–153] that the C=C bond is broken in the oxidation of ethylene by oxygen atoms and that products characteristic of the combustion of methane are formed. This makes it possible to construct a theoretical scheme for the combustion of a weak ethylene–oxygen mixture which is sufficiently complete for the description of the yields of all the main reaction products.[57] A broader and more detailed mechanism of the reaction, necessary for the description of the combustion of rich mixtures, remains, however, outside such a scheme.

The most probable primary steps in this reaction involve the interaction of C_2H_4 with oxygen atoms and hydroxylradicals. The former is apparently the main reaction, since in weak mixtures the concentration of atomic oxygen is usually highest. According to the literature,[151–153] the reaction of C_2H_4 with oxygen atoms proceeds in accordance with the equation

$$C_2H_4+O\rightarrow CH_3+HCO. \qquad (1b)$$

The less important reactions of C_2H_4 have also been less thoroughly investigated. The reaction of C_2H_4 with OH is of this kind and three possible pathways have been proposed for it:[57]

$$C_2H_4+OH\rightarrow CH_3+H_2CO\ , \qquad (2b)$$

$$C_2H_4+OH\rightarrow CH_4+HCO\ , \qquad (2b')$$

$$C_2H_4+OH\rightarrow C_2H_3+H_2O\ . \qquad (2b'')$$

Analytical data have shown[151] that the formation of acetylene C_2H_2 and of the vinyl radical C_2H_3 has been observed in the combustion of ethylene. As already mentioned, the main pathway in the reaction of C_2H_4 in weak mixtures apparently leads immediately to the rupture of the C=C bond, it follows that the formation of C_2H_2 and C_2H_3 is a side process. For this reason, without risking the distortion of the overall picture of the oxidation of C_2H_4, one may attempt to describe in a general form the kinetics of their formation and consumption which have been investigated to only a fairly slight extent. Certain possible reaction pathways, proposed previously by various investigators, were selected for a quantitative test,[57] namely the formation of C_2H_3 via reactions (2b″) and

$$C_2H_4+H\rightarrow C_2H_3+H_2\ , \qquad (-3b)$$

$$C_2H_4+O_2\rightarrow C_2H_3+HO_2 \qquad (-4b)$$

and its consumption via the reactions

$$C_2H_3+O\rightarrow CH_3+CO\ , \qquad (6b)$$

$$C_2H_3+OH\rightarrow CH_3+HCO\ , \qquad (7b)$$

$$C_2H_3+H \rightarrow C_2H_2+H_2\,, \qquad (8b)$$

$$C_2H_3+O_2 \rightarrow C_2H_2+HO_2\,. \qquad (9b)$$

The possible ethylene decomposition reaction

$$C_2H_4+M \rightarrow C_2H_2+H_2+M\,. \qquad (-5b)$$

must be added to the last two reactions, which lead to the formation of acetylene.

The Arrhenius parameters of the reaction rate constants, which in general differ from one another, were known for only three of the processes enumerated above [reactions (1b), (2b), and (5b)]. The values of *A* and *E* for reaction (1b) were taken from Basevich et al.[57], who obtained them by averaging the data from a number of studies;[151–153] those for reaction (2b) were taken from Greiner's data[58] and those for reaction (−5b) were obtained from Kozlov and Knorre[59] (Table 1). Semiempirical estimates were adopted for the remaining reactions. C_2H_2, CH_4, CH_3, H_2CO, HCO, CO, H_2, HO_2, and H_2O, whose further reactions were considered above, are formed in the reactions enumerated. For this reason, the subsequent part of the mechanism involves the DKM for acetylene and methane [in the study of Basevich et al.[57] these were reactions (1b)–(9b), (1d), (2d), (5d), (1)–(14), (14a), (17), (17a), (17d), (19), (21), (24), (26), (27), (28), (29a), (30), (31)–(35), (38), (39), (40), (42)–(45), (46a), (47), (48), (50), (53)–(57), (59), (65), (66)–(69), (70), (70a), (71), (72), (74), (83), (86) from Table 1].

The kinetic curves were calculated[57] for the experimental conditions adopted by Peeters and Mahnen,[151] who provided the most detailed data on the compositions of the ten final and intermediate products generated in a planar ethylene plane. The conditions in these experiments were as follows: $[C_2H_4]_0 = 6.55\%$, $[O_2]_0 = 33.45\%$, $P = 0.0535$ atm, and $T = 1900$ K. The calculated and experimental concentrations agreed in order of magnitude, the agreement being best on the assumption of a single channel in reaction (2b). Hence one may conclude that the reliability of the reaction mechanism underlying the calculation is fairly high.

Naturally the analytical results depend to a large extent on the choice of the reactions and rate constants; however, despite this they are of interest. The contributions of different elementary processes can be most conveniently estimated from the integral *I* [see Eqn.(V)]. The main pathway leading to the consumption of ethylene is, as was in fact assumed, reaction (1b); reaction (2b) has the lowest rate. The replacement of reaction (2b) by (2b′) makes the calculated concentration of methane higher by almost two orders of magnitude. The reaction pathway (2b″) yields a calculated concentration $[C_2H_3]$ twenty times higher than the experimental value. If account is taken only of the interaction of C_2H_4 with O and OH [reactions (1b) and (2b)] and at the same time all the processes associated with the reactions of C_2H_3 and C_2H_2 [(3b)–(9b), (1d), and (2d)], then one obtains in this instance the concentrations of products which agree in order of magnitude with their experimental values {naturally in this calculation it is assumed that $[C_2H_3] = [C_2H_2] = 0$}.

The main process responsible for the appearance of acetylene is

$$C_2H_4+M \rightarrow C_2H_2+H_2+M\,, \qquad (-5b)$$

while the reaction

$$C_2H_4+H \rightarrow C_2H_3+H_2 \qquad (-3b)$$

is responsible for the appearance of the C_2H_3 radical. The main processes leading to their consumption are respectively

$$C_2H_2+O \rightarrow CH_2+CO \qquad (1d)$$

and

$$C_2H_3+O_2 \rightarrow C_2H_2+HO_2\,. \qquad (9b)$$

It is important to note that the fastest branching process under the given conditions, as in the vast majority of cases of high-temperature oxidation of hydrocarbons, is the reaction

$$H+O_2 \rightarrow OH+O\,, \qquad (-4)$$

while the main source of hydrogen atoms is the process

$$HCO+M \rightarrow H+CO+M\,. \qquad (-66)$$

Examination of the overall results of the calculations and their comparison with kinetic data for methane and acetylene flames apparently permit the conclusion that the mechanisms of the combustion of various hydrocarbons are very similar and that hydrogen plays an important role as an intermediate oxidation product.

The kinetic mechanism of the combustion of ethylene has also been considered in other communications,[117,137,154,155] etc.

5. The Combustion of Ethane

The search for reaction schemes describing the combustion of all the more complex hydrocarbons (C_2H_6, C_3H_8, etc.) is important for both chemical kinetics and for practical purposes. The proposed mechanisms are apparently still not yet sufficiently schematic and are conventional in character. The mechanism of the combustion of ethane must naturally include the scheme for the oxidation of yet another stable intermediate—acetaldehyde.

At an early stage of the development of the DKM, two more or less detailed mechanisms of the combustion of ethane were proposed and analysed quantitatively. In one of them,[156] the dissociation of the carbon–carbon bond with formation of methyl radicals was considered as the primary step:

$$C_2H_6 \rightarrow CH_3+CH_3\,. \qquad (-2c)$$

The formation of CH_3 is characteristic also of the oxidation of methane. The author[156] therefore assumed that the subsequent reactions fully correspond to the mechanism of the oxidation of CH_4. The arbitrary nature of this solution is evident, because the rate of decomposition of C_2H_6 can in general be lower than the rate of its reaction with the principal active centres of the reaction—the hydroxylradical OH and the H and O atoms. In a second study[157] the primary reactions considered in the oxidation of ethane involved its interaction with OH, H, O, and O_2, leading to the abstraction of a hydrogen atom and the formation of hydrocarbon molecules and radicals, which in their turn react in the same way. According to this mechanism,[157] the carbon chain is ruptured only in the interaction of the C_2H_2 and C_2H formed with O and O_2 respectively, which leads to the appearance of CH_2, CO, and CHO. Thus the extremely probable reactions of the ethyl radical, which involve the rupture of the C–C bond or the formation of oxygen-containing species, were altogether excluded from consideration.

The mechanism of the combustion of ethane considered below was proposed by Basevich and Kogarko[64] and is based on the probable analogy of the mechanisms of the combustion of C_2H_6 and CH_4; in it additional allowance was made for a large number of reactions proposed previously by various workers, including those associated with acetaldehyde [Table 1, reactions (2c)–(28c)]. In the first six reactions [reactions (2c)–(7c)], the decomposition of ethane as well as the formation of ethyl radicals are postulated. Next, in contrast to the study of Cooke and Williams,[157] certain possible reaction pathways, involving the interaction of C_2H_5 with OH, H, and O and leading to the rupture of the C–C bond and the formation of alkyl radicals and oxygen-containing species [reactions (8c)–(11c)], were introduced.

When the reaction of C_2H_5 with the O_2 proceeds by analogy with the reaction between CH_3 and O_2, it can afford CH_3CHO and OH or, when the C–C bond is ruptured, H_2CO and CH_3O are formed [reactions (12c) and (13c)]. It has been suggested that CH_3CHO then reacts with dissociation of the C–C bond [reactions (−17c) and (−20c)] and with abstraction of the latter in the unimolecular reaction (−21c) or in reactions with H and O [reactions (22c) and (23c)]. The next group of reactions [reactions (24c)–(28c)] agrees in broad outline with the direction of the transformation via ethylene described by Cooke and Williams.[157]

All the processes described above result in the formation of products (H_2, H_2O_2, H_2CO, HCO, CH_4, CH_3, CH_2, CH_3O, C_2H_4, and CO) which also occur in the mechanisms of the combustion of CH_4, CH_3OH, C_2H_2, and C_2H_4; the list of the elementary processes involved in the oxidation of C_2H_6 should therefore be supplemented by the reactions of the latter compounds.

Table 1 indicates the Arrhenius parameters of the rate constants for the above reactions. The values of *A* and *E* were taken from the literature sources quoted, were selected in the calculations, or were estimated approximately from semiempirical formulae.

At sufficiently high temperatures, the mechanism proposed presupposes the occurrence of a branched chain reaction, hydrogen playing the role of the intermediate ensuring degenerate branching.

Calculations[64] have been carried out for two main versions. In the first account was taken of all the reactions involved in the mechanism. In order to elucidate whether the ethane dehydrogenation pathway[157] is the rate determining pathway in ethane combustion and whether the experimentally observed reaction products can be formed, in principle, without following this pathway, in the second version of the calculation all the reactions of the ethyl radical leading to the formation of ethylene were excluded. For the eight products investigated, a qualitative agreement has in general been observed between calculation and experiment.

The published literature data make possible an additional test of the mechanism considered. It follows from the theoretical analysis of the results of experimental studies of the atomic oxygen flame of ethane,[158] the oxidation of $CH_3.CHO$,[159,160] and the ignition delays[157,161,162,163] that the oxidation pathway involving the reactions of C_2H_5 with dissociation of the C–C bond and the formation of alkyl radicals and oxygen-containing species is entirely feasible, like the dehydrogenation pathway. The simultaneous occurrence of the reaction via both channels is extremely likely; however, it is difficult to trace the details of the process by observing the overall kinetics. Judging from the value of the integral *I*, the main substances participating in the reaction (substances whose concentrations are comparable in order of magnitude with the concentrations of the initial compounds consumed and of their reaction partners) are, according to the second version of the calculation, C_2H_6, OH, H, O, HO_2, HCO, CH_3, H_2, H_2O, H_2O_2, CO, CO_2, H_2CO, C_2H_5, O_2, and CH_4. Considerations of the values of *I* permits the conclusion that ethane is consumed mainly in its reaction with OH, H, O, and M. On self-ignition at low temperatures, the highest branching rate is given by the process

$$H_2O_2+M\rightarrow OH+OH+M, \tag{-28}$$

while at high temperatures (>1200 K) the reaction is

$$H+O_2\rightarrow OH+O. \tag{-4}$$

The dissociation of the C–C bond in the atomic flame takes place via the reaction

$$C_2H_5+O\rightarrow CH_3+H_2CO, \tag{11c}$$

while in the remaining cases it occurs in the reactions of C_2H_5 with O_2 and OH and in the decomposition of CH_3CHO. Atomic hydrogen is formed in the reaction

$$O+OH\rightarrow O_2+H \tag{4}$$

or in the decomposition of the formyl radical,

$$HCO+M\rightarrow H+CO+M, \tag{-66}$$

while molecular hydrogen is formed in the reaction of H with C_2H_6, CH_4, and H_2CO. Water appears as a result of the reactions of C_2H_6, H_2, and H_2CO with OH; carbon monoxide is produced by the reaction of HCO with O_2 and M, and carbon dioxide is formed by the reaction of CO with OH and HO_2. Thus the reaction mechanism is in many respects similar to the mechanism of the combustion of CH_4, by analogy with which it has in fact been constructed.

The lack of experimental data at the present time precludes a rigorous selection of the reaction pathways and of all the elementary steps. Table 1 does not include many of the known reactions. There is no doubt that the mechanism discussed must be regarded as preliminary, requiring confirmation and refinement on the basis of a wide variety of experimental data.

The kinetic mechanism of the combustion of ethane has also been analysed in other studies,[137,164,165] etc.

IV. NITROGEN-CONTAINING COMPOUNDS

Methylamine is the simplest amine among those used in the combustion technology independently or as a fuel additive. The knowledge of the mechanisms of the combustion of such compounds is essential for the description of the energy evolution and for the understanding of the kinetics of the formation of the final products, some of which are environmentally undesirable.

The H–C–N–O system is very complex but the availability of data on the kinetics of the combustion of H_2 and C_1–C_2 hydrocarbons with O_2 justifies attempts to construct the combustion mechanism also in this involved case. The construction of a mechanism of the combustion of methylamine is considered below in relation to the atomic oxygen flame.[69] The initial endeavour of the authors[69] to make do with a small number of reactions was unsuccessful; for this reason, subsequently their efforts were directed to the construction of a more or less detailed mechanism.

By analogy with many of the known reactions involving oxygen atoms, one can assume that the abstraction of a hydrogen atom from the molecule being oxidised is extremely probable in the primary step. The C–H bond (93.7 kcal mol^{-1}) is stronger than the N–H bond (87.2 kcal mol^{-1}).[166] One can therefore postulate that the hydrogen abstraction reaction proceeds in accordance with the equation

$$O+CH_3NH_2\rightarrow CH_3NH+OH. \tag{2.1}$$

The hydroxylradical formed in reaction (2.1) and the atomic hydrogen obtained via the reaction

$$O+OH\rightarrow O_2+H \tag{4}$$

can react with the initial molecules in the processes

$$OH+CH_3NH_2\rightarrow CH_3NH+H_2O, \tag{2.2}$$

$$H+CH_3NH_2\rightarrow CH_3NH+H_2. \tag{2.3}$$

The reactions involving the generation of active centres, i.e.

$$CH_3NH_2\rightarrow CH_3+NH_2, \tag{-2.4}$$

$$CH_3NH_2+O_2\rightarrow CH_3NH+HO_2. \tag{-2.5}$$

may be important for self-ignition at high temperatures and in the presence of O_2. Further reactions can be represented only very tentatively. Atomic oxygen and also H, OH, and O_2 can give rise ultimately to species of the type CH_3, CH_3O, CH_4, HNO, NH, and NH_2 on interaction with CH_3NH. However, there are no objective criteria which would make it possible to discover, on the basis of the available experimental data, the processes leading to their formation. For this reason, the reactions presented below should probably be regarded as overall processes:

$$CH_3NH+O \rightarrow CH_3O+NH\ , \qquad (2.6)$$

$$CH_3NH+OH \rightarrow CH_4+HNO\ , \qquad (2.7)$$

$$CH_3NH+H \rightarrow CH_3+NH_2\ , \qquad (2.8)$$

$$CH_3NH+O_2 \rightarrow CH_3O+HNO\ . \qquad (2.9)$$

Starting with the set of species formed in these reactions, it is possible to formulate the subsequent processes (they are also included in Table 1). The reactions of CH_4 and CH_3 in the presence of atomic oxygen were considered earlier in the methane oxidation scheme and, together with the corresponding parameters, they can be usefully adopted as a component of the mechanisms investigated. This also applies to the reactions of the CH_3O radical.

The reactions of the NH, NH_2, and HNO species formed in the processes enumerated above have also been frequently considered by various investigators (for example, by Albers et al.[78]). The rate constants for some of them are known and are presented in Table 1 [see reactions (2.10) to (2.27)]. They include processes involving the possible formation of NH_3. This part of the scheme should describe also the oxidation of NH_3 constituting, together with the reactions in the H–O system, an important part of the DKM for the H–N–O system.

The combustion of rich mixtures of hydrocarbons, particularly nitrogen-containing hydrocarbons, is known to be accompanied by the formation of HCN and NH_3.[167] HCN is formed in large amounts also when NH_3 is added to hydrocarbons. Consequently one may assume that the interaction of the NH_2, N, and NH species, characteristic of the combustion of ammonia, with intermediates in the combustion of hydrocarbons, can also lead to the formation of HCN, as in the combustion of amines, including CH_3NH_2. Part of the kinetic scheme describing the formation of HCN and its oxidation reactions actually corresponds tentatively to this feature [see Table 1, reactions (2.28)–(2.40)].

Reactions (2.41) and (2.42), put forward by Fenimore,[167] make it possible to explain the formation (in the reverse reaction) of HCN and the so called "fast" NO in hydrocarbon flames. On the one hand, atmospheric nitrogen and, on the other, the CH_2 and CH species participate in these processes. The first species occurs in the methane oxidation scheme; the appearance of the second and its consumption were described by reactions (95)–(99), which constitute the continuation of the methane part of the scheme (see the first half of Table 1). The Arrhenius parameters of these processes are indicated on the basis of the estimates of Basevich et al.[50]

Processes responsible for the formation of NO in the high-temperature oxidation of methane in air [reactions (1.12) to (1.15)] (the so called extended Zel'dovich mechanism[168]) are characteristic of this species. Reactions (1.3)–(1.10) take place over a wide temperature range and lead to the formation and decomposition of NO.[89] Reaction (1.11) should also be apparently included here.

Basevich et al.[69] used as far as possible the rate constants for the forward or reverse reactions available in the literature (for the relevant references, see Table 1); in certain cases the Arrhenius parameters were estimated semiempirically. After the initial selection, the parameters listed in Table 1 were used in all subsequent calculations.

The mechanism examined was used[69] in the calculations of the kinetics of the combustion of CH_3NH_2 in an atomic oxygen flame and a fairly satisfactory agreement between experiment and calculations was achieved.

The proportions of the principal reaction products (other than CH_3NH_2, O, and O_2), whose final concentration amountec to not less than 10% of the CH_3NH_2 consumed, can be calculated. These products include H_2, CO , H, CH_4, NO, H_2O, H_2CO, N_2, and NH_3, which are thus the principal species of the kinetic scheme for the given conditions.

Next, the contribution of each elementary step to the reactions of CH_3NH_2 and the individually selected reaction components was calculated.[69] The primary reaction (2.1) involves the consumption of 12–20% of oxygen atoms. The relative contribution of reactions (2.2) and (2.3), involving the consumption of CH_3NH_2 by reaction with OH and H, to its overall reaction is 22–45%. Nitric oxide is formed mainly via the reactions

$$N+OH \rightarrow NO+H\ , \qquad (1.15$$

$$N+O_2 \rightarrow NO+H\ , \qquad (1.13$$

and also

$$HNO+O \rightarrow NO+OH\ , \qquad (2.21$$

$$NH+OH \rightarrow NO+H_2\ . \qquad (2.23$$

The contributions of these reactions diminish in the above order but have similar magnitudes. The contributions of the reactions

$$CH_3+N \rightarrow HCN+H_2\ , \qquad (2.29)$$

$$CH_2+NH \rightarrow HCN+H_2 \qquad (2.28$$

to the formation of HCN are also virtually within the limits of one order of magnitude. In the processes indicated above, the reactions

$$NH+H \rightarrow N+H_2\ , \qquad (2.24)$$

$$NH+O \rightarrow N+OH\ , \qquad (2.25)$$

$$NH_2+NH \rightarrow NH_3+N\ , \qquad (2.16)$$

$$NH+NH \rightarrow NH_2+N \qquad (2.27)$$

play the role of the source of atomic nitrogen. NH_3 is formed via the reactions

$$NH_2+HO_2 \rightarrow NH_3+O_2\ , \qquad (2.11)$$

$$NH_2+H_2 \rightarrow NH_3+H\ . \qquad (-2.18)$$

The rapid reaction

$$NH_2+OH \rightarrow NH_3+O \qquad (2.12)$$

is ineffective owing to the faster occurrence of the reverse process.

A satisfactory agreement has also been found on comparing the calculated and experimental data obtained under the conditions of atmospheric flames[167,169] and experiments with added ammonia.[170]

The insufficiency of experimental data and the complexity of the system considered preclude at the present time a rigorous selection of reaction pathways and all the elementary steps. Table 1 does not include many of the known reactions. There is no doubt that the mechanism discussed should be regarded as a first approximation. This applies especially to the part described by Eqns.(2.6)–(2.9). It is necessary to refine the character of the process and the reaction rate constant.

A kinetic mechanism of the combustion of nitrogen-containing compounds have also been proposed in other studies,[171,172] etc.

The kinetics of combustion in the H–C–N–O system have found an application in the analysis of the environmental consequences of combustion processes and in the search for possible ways of reducing the concentrations of harmful products. Two main reactions leading to the formation of nitric oxide from atmospheric nitrogen [(1.12) and (1.13)] were found to be unspecified in a fundamental study.[168] As already stated, the above mechanism[168] is usually considered jointly with the rapid reaction (1.15). The contribution of reaction (1.15) to the formation of NO has been shown by calculations to be frequently not inferior to the contribution of reaction (1.13) and is sometimes even greater.[173] Under practical conditions, the NO concentration can reach hundredths and thousandths of parts per million owing to the relatively high temperatures and long (more than 0.1 s) residence times of the gas at high temperatures. In the absence of nitrogen in the fuel itself, the above mechanism of the formation of NO is the main one.

Under laboratory conditions, which are distinguished as a rule by low temperatures (<2000 K) and short residence times of the gas (less than 10–20 ms), the yield of NO amounts to several, several tens, and (rarely) 100 parts per million. Under these conditions, the approximations underlying the theory[168] are insufficiently valid and for this reason differences are observed between the theoretical and experimental nitric oxide concentrations: there is insufficient time for the attainment of equilibrium and the actual concentrations of atomic oxygen can exceed significantly those corresponding to thermodynamic equilibrium. Calculations using the DKM have shown that more NO is usually obtained under these conditions.[174–176] However, this applies solely to hydrocarbons. The calculations for hydrogen–air flames have fully confirmed the theoretical and experimental data,[168] which indicates the possibility of excluding the reaction zone from consideration. The calculations have also shown that, up to pressures of 100 atm, the amount of NO formed in the reaction zone of the H_2 flame even at an initial temperature of 600 K is extremely insignificant owing to the short residence times.

Under laboratory conditions, the abrupt formation of nitric oxide in the reaction zone on combustion of hydrocarbons was first observed by Fenimore.[173] It was noted that, under the experimental conditions, the formation of NO includes two stages: the rapid stage in the reaction zone and the slow stage in the flame gases. The mechanism of the formation of NO via reactions (1.12)–(1.15) operates in both stages. The authors[177] concluded that in the case of hydrocarbons the mechanism (1.12)–(1.15) describes the combustion of weak mixtures with a coefficient of the excess of air $\alpha \geq 1.3$.

Data for rich mixtures with a large discrepancy between the unduly low calculated and experimental NO concentrations, indicating that the mechanism of the formation of nitrogen oxide is in this instance apparently more complex and is not confined to the scheme (1.12)–(1.15), have been frequently quoted in the literature. Special experiments have been carried out,[178] in which the yields of NO were compared under identical conditions in hydrogen–oxygen–nitrogen flames without and with addition of acetylene. In the latter case more nitric oxide is formed and there is reason to believe that its formation is promoted by the reactions of hydrocarbon radicals with nitrogen (Table 1, DKM for the H–C–N–O system), although these NO formation pathways have not as yet been adequately investigated. We may note that the concentrations of "fast" NO do not exceed 100 to 120 p.p.m.[179] In the latter studies the authors specially optimise the experimental conditions in order to obtain the maximum yield of this species.

Finally, there exists yet another source of the formation of nitrogen oxides on combustion. This is the nitrogen which forms part of the composition of fuel and impurity molecules. Experiments have shown[180] that, depending on the combustion conditions and the composition of the fuel mixture, between 10 and 90% of the fuel nitrogen is converted into nitric oxide; the remainder (in rich mixtures) forms ammonia and HCN as well as nitrogen molecules (see the above scheme for the H–C–N–O which was formulated to account for the formation of NO from the fuel nitrogen, requires a more detailed specification and justification. The possible role of N atoms in this process, which have been discovered by Basevich et al.[69], has also been pointed out by Miller et al.[172]

V. THE APPLICATION OF H_2O_2 AND HNO_3 AS OXIDANTS

The use of hydrogen peroxide as oxidants instead of oxygen is based on the relative ease of its thermal decomposition with formation of two hydroxylradicals. The oxidation of the corresponding mixtures begins at the temperature of the onset of appareciable decomposition of hydrogen peroxide.[9] It was stated above that hydrogen peroxide is an essential component of the DKM of the oxidation of hydrogen and hydrocarbons and the kinetic mechanism where H_2O_2 functions as the oxidant is therefore identical with the mechanism of the reaction in the oxygen system.

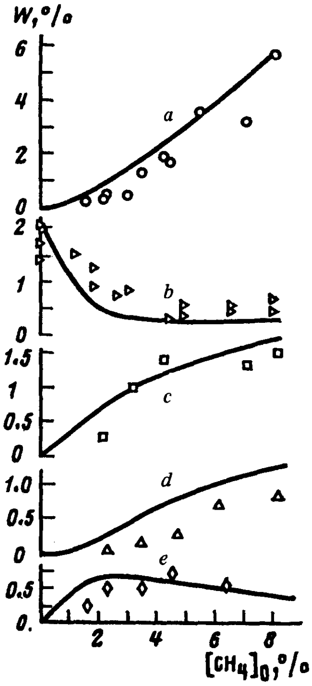

Figure 4. Dependence of the yield of the products of the reaction of CH_4 with HNO_3 on the initial methane concentration;[88] $[HNO_3]_0 = 7\%$, $T = 1067$ K, $P = 0.01$ atm, $t = 5$ ms: symbols—experiment; lines—calculation; *a*) CH_4; *b*) NO_2; c) CO; d) H_2; *e*) CO_2.

The calculated and experimental data were compared under flow conditions for the CH_4–H_2O_2 [33] and H_2–H_2O_2 [28] systems. The presence of a certain initial concentration $[O_2]_0$ as a consequence of the presence of O_2 in liquid H_2O_2, which, when vaporised by bubbling, generated the necessary H_2O_2 concentration in the gas phase, was noted in the experiments. A satisfactory agreement between the experimental and calculated data was achieved in both cases.

Nitric acid also readily decomposes with formation of nitrogen dioxide and a hydroxylradical[181,182] and is therefore used as the oxidant.[183,184] The hydroxylradical obtained reacts again with nitric acid to form the highly reactive NO_3 radical and water [reactions (1.1) and (1.2) in Table 1]. Examination of the above processes together with the DKM for the H—N—O system made it possible to analyse the kinetics of the interaction of hydrogen with nitric acid.[28] The reaction proceeds fairly rapidly but, as a consequence of the high rate of destruction of OH, H, and O in the gas samples of the EPR spectrometer due to the presence of nitrogen-containing products, the concentration of these radicals could not be recorded.

Certain experimental data referring to the reaction of CH_4 with HNO_3 under flow conditions are presented in Fig.4.[88] The reaction begins at the temperature corresponding to the onset of the decomposition of HNO_3. The calculated kinetic curves describe satisfactorily the experimental relations obtained when the initial methane content is varied.

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The theoretical studies described above were not the only ones performed with the aid of the DKM. They have been used to calculate the ignition delays, the rates of propagation and the stabilisation limits of flames, in the study of promotion and chemi-ionisation phenomena and of the composition of the products in the technological formation of acetylene and the synthesis gas from methane, in the estimation of the concentrations of various environmentally undesirable components, and in other cases, including the conditions in a turbulent medium. The results of the available calculations demonstrate their more or less satisfactory agreement with experimental data. The specific DKM presented in Table 1 serves merely as the first approximation and requires further refinement.

The first stage in the construction of the detailed kinetic mechanisms, where their possibilities and the accuracy of the calculations based on them have become clear has apparently now been completed. The next stage in the construction of the DKM will probably involve a careful analysis of the individual elementary steps and the real reaction channels and also an increase in the accuracy of the estimation of the rate constants. The aim of this stage will be a transition from qualitative estimates obtained nowadays to a quantitatively accurate *a priori* calculation.

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A Quantitative Concept of the Permeability to Hydrogen of Passivating Layers on a Metal at the Apex of the Crack in the Corrosion-induced Cracking of Constructional Materials

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A general theoretical and methodological approach to the determination of the role of the local anodic dissolution and hydrogen-induced embrittlement in the corrosion-induced cracking of various constructional materials is examined. The possibility of the quantitative estimation of the role of the hydrogen-induced embrittlement in the corrosion-induced cracking of high-strength steels and titanium, aluminium, magnesium, and zirconium alloys is demonstrated. A quantitative concept of the permeability of hydrogen of passivating layers on a metal at the apex of a crack, which has made it possible to determine quantitatively for the first time the relation between the critical concentration of hydrogen and the stress intensity coefficient in the hydrogen-induced embrittlement of steels and titanium and aluminium alloys, has been developed on the basis of several postulates. Two new methods for the investigation of the adsorption of hydrogen and anions at the apex of the crack in corrosion-induced cracking, based on this concept, are proposed.

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I. INTRODUCTION

There is at present no unique concept concerning the mechanism of the growth of cracks in corrosion-induced cracking (CIC) on any specific alloy—electrolyte system. There is an even greater lack of a generally accepted theoretical and methodological approach to the determination of the mechanism of the growth of cracks which would be applicable to any constructional materials regardless of their composition and structural state. The majority of studies have been characterised by a one-sided approach to the determination of the CIC mechanism—whilst justifying the leading role of one of the possible mechanisms, the authors fail to consider or reject the possibility of the growth of cracks via other, competing mechanisms. An attempt has been made[1-3] to develop a general electrochemical method for the determination of the CIC mechanism using the following initial postulates. At the apex of the crack there is a possibility of the simultaneous occurrence of two main processes—local anodic dissolution (LAD) and hydrogen-induced embrittlement (HIE), the role of each of which depends on the composition of the alloy and the electrolyte, the heat treatment of the alloy, the potential, etc. and also on the rate of growth of the crack V and the stress intensity coefficient K. The coefficient V is regarded as an index of the extent to which the properties of the metal at the apex of the crack approach those of a freshly formed surface and defines the permeability of the passivating films to hydrogen. The different types of influence of cathodic polarisation on the growth of cracks observed in the study of high-strength martensite steels[1] serve as an experimental basis of the ideas concerning the CIC mechanism developed in the above studies.[1-3] This phenomenon consists in the fact that, other conditions being equal, the same cathodic polarisation retards the growth of cracks if the initial V and K at the corrosion potential are below certain critical values and accelerates the growth of cracks if they are above such values. The physical significance of the concept of the "critical rate of growth of the crack" is as follows. With increase of V, the time required for the formation of passivating layers on the metal at the top of the crack, which constitute barriers to the penetration of hydrogen into the metal, diminishes. Regardless of the value of V, cathodic polarisation increases the rate of the electrochemical evolution of hydrogen. However, for coefficients V below the critical value, the films formed on the metal hinder the penetration of hydrogen into the latter, the attainment of the critical concentration of hydrogen, and the onset of the HIE. On the other hand, cathodic polarisation suppresses the LAD and, as shown by experiment, reduces V. When the critical and higher values of V are reached, passivating films can no longer effectively prevent the penetration of hydrogen into the metal and for this reason cathodic polarisation accelerates the growth of cracks via the HIE mechanism although it does reduce the rate of local dissolution.

The critical rate of growth of the crack V_{cr} and the corresponding critical stress intensity coefficient K_{HIE} are quantitative indices of the role of the LAD and HIE in the growth of the cracks; for $V < V_{cr}$ and $K < K_{HIE}$, the main CIC mechanism involves the LAD; for $V > V_{cr}$ and $K > K_{HIE}$, the mechanism is based on the HIE. The values of V_{cr} and K_{HIE} depend on the composition of the alloy and the electrolyte, the cathodic polarisation potential, etc. Changes in the alloy—electrolyte system reducing the stability of the passivating layers at the apex of the crack or the critical concentration of hydrogen should diminish V_{cr} and K_{HIE}, i.e. should enhance the role of the HIE in the CIC. This hypothesis was confirmed experimentally in the determination of the dependence of V_{cr} and K_{HIE} in the CIC of high-strength steels on the content in the electrolyte of chlorides, agents promoting such saturations with hydrogen, and oxidants and also the dependence of these quantities on the heat treatment of the steels.[1,2]

Although the ideas which we have developed[1–3] about the CIC mechanism suffer from no limitations associated with the composition of the alloy or the electrolyte, they cannot be transferred mechanically to all materials without demonstrating experimentally that cathodic polarisation exerts different types of influence on the growth of cracks in the CIC of these materials, as for high-strength steels. As the above ideas were generalised, they were subjected to tests. In particular, it was assumed *a priori* that, when any alloy (or group of alloys with a specific base) tends to undergo HIE in the absence of a corrosion medium but at the same time cathodic polarisation always has the same effect on its CIC, it is possible to alter the CIC conditions in such a way that cathodic polarisation exerts different types of effect on V for this alloy. For example, it is known that austenite steels and titanium, zirconium, magnesium, and alluminium alloys tend to undergo internal HIE but, in CIC in 0.5 M NaCl solution, cathodic polarisation only retards the growth of cracks in these materials.[2] This means that in the NaCl solution the main CIC mechanism involves LAD, while HIE does not play an appreciable role although it can occur. On the other hand, one can postulate the existence of conditions for these materials such that HIE plays an appreciable or main role in the CIC. Indeed electrolytes have been selected in which cathodic polarisation in the CIC of the above materials influenced the growth of cracks in different ways; for V and K below their critical values, it reduced V, increasing it after the attainment of such values.[2–4]

The agreement between the theoretical prediction and the experimental fact of the different types of influence of cathodic polarisation on the growth of cracks in the CIC of austenite high-strength steels and titanium, zirconium, magnesium, and aluminium alloys[2–4] suggests that this feature is common to all CIC processes and makes it possible to formulate a general theoretical and methodological approach to the determination of the role of LAD and HIE in the CIC of constructional materials regardless of their base and the composition of the electrolyte. According to this approach, the unambiguous influence of cathodic polarisation (i.e. only retardation or only acceleration of the growth of cracks regardless of the values of V and K) should be regarded as a special case of its varying influence on V, reflecting the independence of the leading CIC mechanism of V and K. More detailed arguments in support of this postulate can be found in another communication.[2]

The ideas about the CIC mechanism developed in a series of studies[1–4] are mainly qualitative. In the present review a quantitative concept of the permeability to hydrogen of passivating layers on a metal at the apex of the crack, which makes it possible to establish a relation between the electrochemical CIC conditions, the coefficients V_{cr} and K_{HIE}, and the critical concentration of hydrogen in the HIE, has been formulated on the basis of the extension and analysis of these ideas.

II. RELATION BETWEEN THE CRITICAL CONCENTRATION OF HYDROGEN AND THE CRITICAL STRESS INTENSITY COEFFICIENT IN THE HYDROGEN-INDUCED EMBRITTLEMENT OF CONSTRUCTIONAL MATERIALS

The fundamental concepts of the theory of the HIE of constructional materials are the critical concentration of hydrogen c_{cr} and the critical stress intensity coefficient in HIE, K_{HIE}. The value of K_{HIE} can be determined experimentally both in the HIE in gaseous hydrogen and in electrolyte solution under CIC conditions. However, none of the methods of physicochemical analysis and none of the HIE theories have so far been developed sufficiently to permit the experimental or computational determination of the absolute values of c_{cr} (there is no generally accepted physical model of the HIE; models of the distribution of stresses ahead of the apex of the crack are in the state of development; the configuration of the apex of the crack and the location of the breakdown zone in the HIE relative to the top of the crack are unknown, etc.[2,5]). The question of the relation between c_{cr} and K_{HIE} is extremely important for the theory of HIE and was frequently discussed previously.[2,5–9] However, at the present time only the following qualitative relation can be regarded as established: the higher K_{HIE}, the lower c_{cr} and conversely.

The method for the investigation of the relation between c_{cr} and K_{HIE} proposed by the present author[10] follows from general ideas about the CIC mechanism[1–4] and is based on the possibility of the quantitative estimation of the role of HIE in CIC by means of the experimental determination of the values of V_{cr} and the corresponding critical stress intensity coefficients K_{HIE}. These values depend on the electrolyte composition, the heat treatment and the structure and strength of the alloy, the pH of the medium, the presence of agents promoting saturation with hydrogen, the process temperature, the potential of the specimen, and also the nature and the ratio of the concentrations of the corrosive and passivating ions. The last factor is particularly important because this ratio defines, like V, the permeability to hydrogen of the film of the metal at the top of the crack.

The main postulate of the HIE theory states[2] that the crack grows when the critical hydrogen concentration c_{cr} is established ahead of its apex and the critical value of the stress intensity coefficient K_{HIE} has been attained. Having supplemented this condition by stating that c_{cr} decreases with increase of K_{HIE}, one can formulate the equation

$$c_{cr}K_{HIE}^{n} = \text{const.} \tag{1}$$

This relation, proposed in Ref.11, is one of the possible formulations of the criterion of breakdown in HIE and is not based on any specific physical model of HIE. Formally it is close to the power relation examined by Van Leeuwen[9] within the framework of the decohesive theory of HIE.[8]

The penetration of hydrogen into the metal ahead of the apex of the crack growing under the CIC conditions includes several successive steps:

(1) The occurrence of an electrochemical reaction as a result of which a definite concentration (degree of surface coverage) of adsorbed hydrogen atoms θ is established on the surface of the passivating film.

(2) The penetration of the hydrogen adsorbed on the surface of the film through the latter and the establishment of a certain concentration c_{ms} of hydrogen in the surface layer of the metal at the apex of the crack at the metal–film boundary. This concentration is determined by the permeability of the film to hydrogen: $c_{ms} = \theta\alpha$. The dimensionless quantity shows what proportion of the hydrogen adsorbed on the passivating film penetrates through the latter and is responsible for the HIE.

(3) The attainment of a critical concentration of hydrogen $c_{cr} = c_{ms}\xi = \theta\alpha\xi$ directly at the apex of the crack ($\xi = 1$) or at a certain distance from it ($\xi < 1$), the distance being unimportant, since the given formal treatment is not associated with any specific physical model of HIE. The requirements that the HIE mechanism remains unaltered when the experimental conditions are changed (for example, when the cathodic polarisation potential or the concentration of chloride ions are changed) and that the transport coefficient ξ remains constant are significant.

The HIE mechanism is determined by the properties of the metal–hydrogen system and is independent of the electrochemical conditions at the apex of the crack which influence the HIE kinetics in CIC. The coefficient ξ depends on the diffusion coefficient of hydrogen in the metal, the distance of the breakdown zone from the apex of the crack, and the diffusion time, i.e. on the duration of the cathodic polarisation in the determination of the values of K_{HIE}. For a constant cathodic polarisation time, ξ = const. for the given alloy.

The constancy of the cathodic polarisation time is ensured by the method used to determine K_{HIE},[10] which consists of the following steps. The specimen in the electrolyte at a certain initial potential E_i (for example the corrosion potential E_{cor}) is stressed until the attainment of an arbitrary coefficient K, is maintained in this state for 300 s, and is then subjected to cathodic polarisation until the attainment of the potential E_{cp}. If the cathodic polarisation induces an acceleration of the growth of the crack up to 150 s, the specimen is again polarised to E_i, K is reduced by 3–5%, and, after being maintained at E_i the specimen is polarised to E_{cp}. If the cathodic polarisation does not accelerate the growth of the crack in the course of 150 s, then K is increased by 3–5% and the above operations are repeated. Thus, using the method of successive approximations, K_{HIE} is determined as the minimum value of K for which cathodic polarisation to E_{cp} accelerates the growth of the crack up to 150 s. The relative errors in the determination of K_{HIE} and V_{cr} are 4 and 10% respectively.[10]

The quantities θ and α depend on the compositions of the alloy and the electrolyte, the pH, temperature, the potentials E_i and E_{cp}, etc. Other conditions being equal, the permeability to hydrogen is proportional to the rate of growth of the crack and the concentration of the corrosive anion, for example the chloride ion $[Cl^-]$, adsorbed on the film at the top of the crack. It is assumed that the adsorption of chloride ions from solution is described by the Langmuir isotherm at low coverages: $[Cl^-] = \beta(Cl^-)$, where β is the adsorption coefficient and (Cl^-) and $[Cl^-]$ are the concentrations of chloride ions in solution and adsorbed on the film respectively. It is also assumed that, when $V \leq 0.01$ mm h^{-1}, the permeability of the film to hydrogen is independent of the rate of growth of the crack and, when $V > 0.01$ mm h^{-1}, it is proportional to V.[10]

These ideas about the permeability to hydrogen of passivating films on the metal on top of the crack growing under CIC conditions are based on the present author's data;[2,3] in the absence of halide ions, it proved impossible to induce the HIE of aluminium, titanium, and zirconium alloys under CIC conditions even for $K \cong K_{IC}$ (where K_{IC} is the critical stress intensity coefficient in the absence of corrosion medium) and a cathodic polarisation potential E_{cp} up to -4 V (relative to n.h.e.†), while for certain ratios of the concentrations of passivator and depassivotor ions optimal for each material the acceleration of the growth of cracks under cathodic polarisation (i.e. HIE and CIC) is observed for $K_{HIE} \leq 0.03$, K_{IC}, and $E = -0.7$ V. For the materials investigated previously,[2,3] the quantity α can be neglected in the absence of corrosive ions, but, for high-strength steels this cannot be done in the general case, since their CIC via the HIE mechanism can occur, for example, in distilled water. However, even for high-strength steels it is possible to establish conditions (by selecting the composition of the electrolyte and the cathodic polarisation potential) under which the permeability of the film to hydrogen is determined by the concentration of the corrosive ions in the electrolyte also at the top of the crack. In this Section only such conditions will in fact be considered; the permeability of steels to hydrogen is discussed in greater detail in Section III.

Taking into account the above assumptions concerning the critical parameters describing quantitatively the role of HIE in CIC (V_{cr} and K_{HIE}, the criterion for the HIE in the alloy–hydrogen system (1) can be used also as the criterion of the HIE in CIC having formulated it in the form

$$\theta\alpha\xi K^n_{HIE} = \text{const}, \tag{2}$$

$$\theta\xi\beta(Cl^-)V_{cr}K^n_{HIE} = \text{const}, \tag{3}$$

$$\lg[(Cl^-)V_{cr}] = \text{const} - n\lg K_{HIE}. \tag{4}$$

The constant coefficients ξ and β in Eqn.(3) are unknown and it is therefore impossible to determine the permeability of the film to hydrogen in absolute units. However, the exponent n in the power relation (1) between the critical concentration of hydrogen and the stress intensity coefficient can be determined from the slope of the linear plot in terms of the variables of Eqn.(4).

In conformity with the assumptions made, the power exponent n in Eqns.(1)–(4) characterises the HIE in the alloy–hydrogen system and is in no way related to the corrosion stability of the alloy in any particular electrolyte. Hence it follows that n may depend on the composition, structure, and the conditions of the heat treatment of the alloy and on temperature but should be independent of any electrochemical parameters of the electrolyte.[10] The experimental test of these conclusions shows that the assumptions made in the derivation of Eqns.(1)–(4) are valid. In particular, the observed value of n should be independent of the method of introduction of hydrogen into the specimen: for the same material, the exponent n should be identical for HIE under CIC conditions and in an atmosphere of gaseous hydrogen. For HIE in CIC, the exponent n should not be influenced by the nature of the solvent, the concentrations of the passivator and depassivator ions, the pH, the cathodic polarisation potential, and similar factors, although variation of these parameters does influence significantly V_{cr}, K_{HIE}, θ, and other terms in Eqns.(2)–(4).

Since n is independent of the electrochemical parameters of the solution, all the data obtained for one material in different solutions may be plotted on a single curve. In each series of experiments where only the concentration (Cl^-) is varied, the solution with the maximum value of (Cl^-) is selected as the standard.[10] Then, for this series, Eqn.(4) is transformed into

$$\lg\frac{[V_{cr}(Cl^-)]_x}{[V_{cr}(Cl^-)]_{st}} = \lg\frac{\alpha_x}{\alpha_{cr}} = -n\lg\frac{K_{HIE,x}}{K_{HIE,st}}, \tag{5}$$

where the subscripts "st" and "x" correspond to the standard in variable concentrations (Cl^-).

The validity of Eqn.(5) was tested in a study[10] in which the dependence of K_{HIE} and V_{cr} on the concentrations of chloride, bromide, and sulphate ions was obtained in various buffer solutions in the CIC of aluminium and titanium alloys and four high-strength martensite steels. These data, treated in accordance with Eqn.(5), are presented in Fig.1; it is seen that, despite the considerable scatter, the experimental points for each material do indeed fit on a straight line. The slopes of the straight lines (i.e. the power exponents n) for the aluminium alloy, the titanium alloys, and the high-strength steels are respectively 2.1, 3.0, and 5.5. As assumed, n for each material is independent of the electrochemical parameters associated with the electrolyte; however, within the limits of experimental error, it was impossible to

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†Here and henceforth the potentials are given throughout relative to the normal hydrogen electrode (n.h.e.).

observe the dependence of *n* not only on the conditions in the heat treatment of the steel but also on the composition, structure, and strength of titanium α-alloys and the high-strength martensite and martensitically ageing steels.

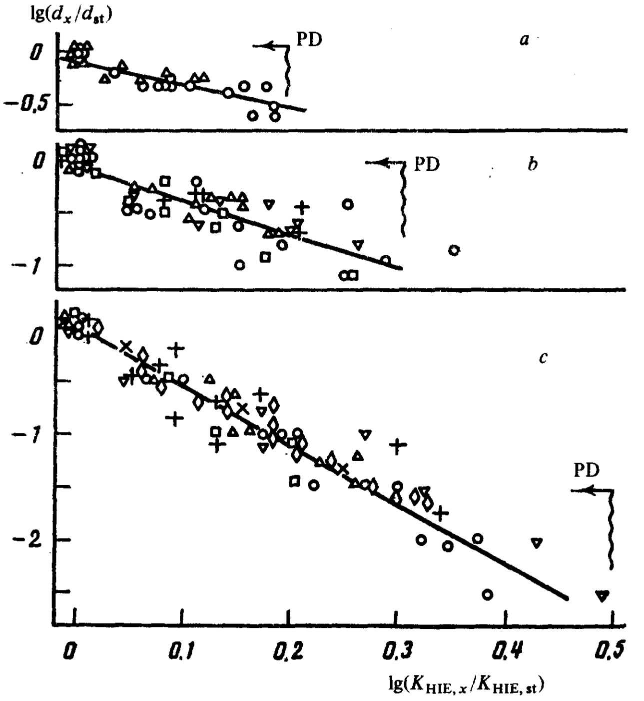

Figure 1. Dependence of K_{HIE} in the CIC of aluminium (*a*), and titanium (*b*) alloys and high-strength steels (*c*) on the permeability to hydrogen of the passivating films at the apex of the crack; PD—planar deformation boundary. The different symbols correspond to different alloys, different heat treatment conditions, and different electrolyte compositions.[10]

One can apparently conclude that the exponent *n* in Eqn.(1) is a characteristic parameter of the HIE of the alloys and depends solely on the nature of the metal on which the alloy is based. One cannot rule out the possibility that the different values of *n* for aluminium and titanium alloys and high-strength steels reflect different mechanisms of the HIE of these materials. We may note that, with increase of the tendency of the materials towards HIE in the series aluminium alloys–titanium alloys–high-strength steels, the exponent *n* also increases. Unfortunately, there are no data concerning the influence of the type of lattice on *n*; such data can be obtained by studying with the aid of the method described titanium β-alloys and high-strength austenite steels.

As stated above, in the model considered the exponent *n* should not be influenced by the method of introduction of hydrogen into the alloy. The validity of this postulate can be tested by comparing the value $n = 5.5$ obtained[10] for high-strength steels (under the conditions of HIE in CIC) with the value of *n* under the conditions of gas-phase HIE. There are fairly numerous literature data on the dependence of the K_{HIE} of high-strength steels on the hydrogen pressure, but they are unsuitable for the determination of *n*, because they refer mainly to the range of high (in excess of 1 atm) pressures at which one can postulate the maximum degree of surface coverage by adsorbed hydrogen atoms. Virtually the only study in which the dependence of K_{HIE} (for high-strength martensite steel 4340) on hydrogen pressure was determined (in the range 0.1–1000 mmHg) is that of Oriani and Josephic.[8] The data from this investigation, treated in terms of Eqn.(5), are designated in Fig.1c by rhombuses; they fall within the scatter band of the HIE data in the CIC of other high-strength steels. The exponent *n*, determined independently from the results of the above investigation,[8] is 5.1 and is virtually identical with the value $n = 5.5 \pm 0.5$ found for HIE in CIC.[10]

Despite the fact that Eqns.(1)–(5) are empirical and are not based on any specific physical model of HIE, the values of *n* obtained[10] can be useful in the development of physical ideas about the mechanism of the HIE of various materials. In particular, the identity of the values of *n* for the HIE in the CIC of high-strength steels and for their HIE in a gaseous medium makes it possible to assume that the HIE of these materials has the same mechanism.

The derivation of Eqns.(1)–(5) is based on several postulates (the applicability of the proposed criterion of breakdown in HIE, the direct proportionality of the permeability to hydrogen to the rate of growth of the crack and to the concentration of chloride ions adsorbed on the film, and the independence of θ of [Cl$^-$], which do not conflict with the known theoretical ideas but cannot be justified analytically or tested experimentally. For example, it is impossible to test by an independent procedure the values of *n* obtained,[10] because only qualitative ideas about the relation between c_{cr} and K_{HIE} have been developed in the HIE theory. Nevertheless the concept of the permeability of passivating layers on the metal to hydrogen at the top of the crack, developed by Marichev,[10] permits predictions for certain values of *n* which can be tested experimentally (see Sections III and IV).

III. THE PERMEABILITY TO HYDROGEN OF PASSIVATING LAYERS ON A METAL AT THE APEX OF THE CRACK IN CORROSION-INDUCED CRACKING

The permeability to hydrogen α was formally introduced above dimensionless quantity showing which part of the hydrogen adsorbed on the passivating film penetrates through it onto the metal–film interface and is responsible for the occurrence of HIE. The mechanism of the permeability to hydrogen has not yet been fully elucidated but one can assume that the diffusional transport of hydrogen through the passivating film does not play the main role. Thus in the CIC of aluminium and titanium alloys for $K > K_{HIE}$ the acceleration of the growth of the cracks after the cathodic polarisation has been switched on takes place after 1 s, while for $K < K_{HIE}$ under the same CIC conditions acceleration was not observed even after more than 10^4 s. Furthermore, the occurrence of the CIC of these alloys via the HIE mechanism, for example, in 1 M CrO_3 has not been observed even for $K \cong K_{IC}$, but, when 0.01 M NaCl is introduced, HIE takes place at a high rate for low values of *K*. It appears unlikely that such small amounts of added chloride ions, which do not alter significantly the corrosion potential and do not cause the breakdown of the passive state of the alloys in 1 M CrO_3 solutions, should increase by several orders of magnitude the diffusion coefficient of hydrogen in the passivating film.

Since θ and the constant coefficients (except *n*) in Eqns. (2) and (3) are unknown, the absolute values of the permeability to hydrogen cannot be determined from data obtained in tests on the CIC (i.e. the quantities V_{cr} and K_{HIE}). However, having adopted $\alpha = 1$ for certain arbitrarily selected standard experimental conditions, it is possible to determine the relative changes in α_x when, for example, the concentration of chloride ions in the electrolyte is altered:

$$\alpha_x = \frac{V_{st}}{V_x}\left(\frac{K_{HIE,st}}{K_{HIE,x}}\right)^n . \qquad (6)$$

It is assumed that small changes in the composition of the electrolyte (as a rule by not more than 0.05 M of activator or passivator ions) do not affect the surface coverage θ of the film by adsorbed hydrogen, which depends mainly on the potential of the specimen and the pH of the electrolyte.[12]

The most complete information about the dependence of the permeability to hydrogen α of passivating layers on a metal at the top of the crack on the electrolyte composition can be obtained for high-strength steels, since in the course of their CIC the growth of cracks via the HIE mechanism at sufficiently negative cathodic polarisation potentials takes place in water and NaOH solutions not containing activating ions.[2] The following standard experimental conditions have been selected[13] for high-strength steels: NaOH solution at pH 10, cathodic polarisation potential for the determination of V_{cr} and K_{HIE} amounting to $E_{cp} = 0.8$ V, and the period from the instant when the cathodic polarisation is switched on to the instant of the acceleration of the growth of cracks via the HIE mechanism amounting to 150 s. This choice was dictated by the necessity to keep constant the pH of the electrolyte as its composition is changed (for example, the 0.03 M Na_2HPO_4 solution has pH 9.9), the appreciably insignificant corrosion of the steels investigated, and also the fact that in this electrolyte the critical HIE stress intensity coefficient is small for $E_{cp} = -0.8$ V. The latter significantly extends the possible limits of variation of the electrolyte composition, especially on introduction of passivators, since the increase of K_{HIE} induced by them should not lead to the breakdown of the passive planar deformation state of the specimens.[14] The corrosion potential of the steels studied was approximately 0.2 V in NaOH solution at pH 10 and −0.15 V in 0.03 M Na_2HPO_4 solution, changing insignificantly (by ±0.05 V) after the introduction of activator or passivator ions into these electrolytes at a concentration of 0.05 M.

Fig. 2 shows that the introduction of additional NaOH at a concentration of 0.03 M into the standard NaOH solution increases the permeability to hydrogen of the passivating films at the apex of the crack by a factor of 6, while the additional introduction of 0.01 M NaCl causes a further increase by a factor of 2. The addition of nitrate ions to these solutions lowers sharply the permeability to hydrogen, the decrease being more pronounced the lower the initial permeability. Thus, when 0.001 M $NaNO_3$ is introduced into the standard solution, the permeability to hydrogen diminishes by a factor of 15 (curve *1*), but it hardly changes when the solution contains also 0.01 NaCl (curve 3).

We must emphasise that not only nitrates but also other anions, mainly oxidants (chromates, nitrites, nitrobenzoates, etc.) can reduce α, but there is no correlation between the strength of the oxidant and the degree of its influence on the permeability to hydrogen. For example, the strongest oxidants investigated by the present author,[13] namely H_2O_2 and $Na_2S_2O_8$, at concentrations up to 0.1 M do not reduce α in the CIC of steel in the presence of 0.03 M Na_2HPO_4 (the latter actually increases significantly α, since its reduction entails the formation of sulphate, which, like the chloride ion, increases the permeability to hydrogen). The introduction into the same solution of 0.05 M $NaNO_3$, which is an appreciably weaker oxidant but effectively displaces chloride ions from the surface of the steel as a result of competitive adsorption,[13,15] lowers α by three orders of magnitude.

It is of interest to compare the role of phosphates and nitrates. Phosphates are assumed to be corrosion inhibitors; indeed in the presence of 0.03 M Na_2HPO_4, the corrosion potential increases by 0.05 V compared with the potential in NaOH and the corrosion of the specimens is almost fully suppressed but the permeability to hydrogen of the passivating layers at the top of the crack increases by 5–6. On the other hand, nitrates are believed to behave as corrosion activators (although there have been studies[16,17] demonstrating their inhibiting effect on the CIC process and corrosion fatigue), but they reduce α very markedly in solutions containing chlorides and sulphates and fully suppress the CIC of high-strength steels in a standard NaOH solution. In a series of prolonged (up to one month) experiments, it was shown that not only K_{HIE} but also K_{ISCC} (critical coefficient of the density of stresses in CIC) increases appreciably in the presence of nitrates.[13]

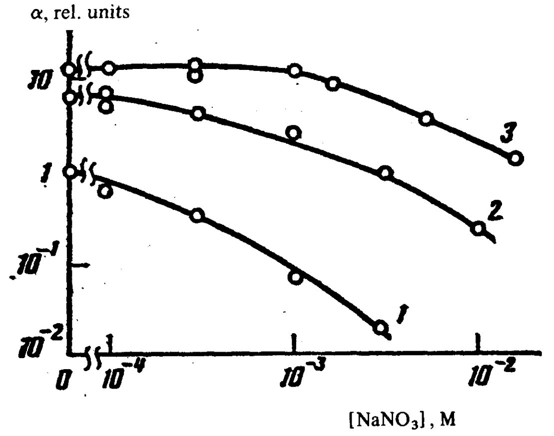

Figure 2. Dependence of the permeability to hydrogen, α, of passivating layers on a metal at the apex of the crack on the concentration of added $NaNO_3$ in the CIC of the steel 33Kh3NMFA in solutions at pH 10: *1*) NaOH; *2*) NaOH + 0.03 M Na_2HPO_4; *3*) NaOH + 0.03 Na_2HPO_4 + 0.01 M NaCl. The permeability to hydrogen in the NaOH solution was adopted as unity; $E_{cp} = -0.8$ V.[13]

It was subsequently established[15] that, when HIE conditions in distilled water are chosen as standard, all the anions investigated—the phosphate, acetate, borate, nitrate, hydroxide, and especially chloride and sulphate ions—increase the permeability of passivating films to hydrogen, i.e. they function as activators of the HIE of high-strength steels. The activating effect of anions on the HIE process depends significantly on the steel composition. Nitrates and other oxidants lower the permeability to hydrogen and increase HIE and hence they function as inhibitors of the HIE process only when they are introduced into solutions containing other anions, for example, chloride or sulphate ions, which activate the HIE of steel to a greater extent than nitrate ions.

One of the consequences of the concept of the permeability of passivating films to hydrogen has been the development of a method of study *in situ* of the adsorption of chloride ions (or other activator ions) on the film at the apex of the crack in the CIC of constructional materials.[15] The method consists in the experimental determination of K_{HIE} and V_{cr} under standard and real conditions and in the calculation of the relative changes in the concentration of chloride ions $[Cl^-]$ at the top of the crack. The standard condition is assumed to be $[Cl^-]_{st} = 1$. The real conditions differ in the concentrations of chloride or nitrate ions in the solution. It has been suggested that the constant coefficients in Eqns.(2) and (3) are identical for standard and real conditions. It follows from Eqns.(2) and (3) that

$$[Cl^-]_x = \frac{V_{st}}{V_x}\left(\frac{K_{HIE,st}}{K_{HIE,x}}\right)^n . \tag{7}$$

Within the framework of the assumptions made above, Eqn. (7) makes it possible to calculate the isotherms for the adsorption of chloride ions on the surface of the passivating film at the top of the crack growing in the CIC and also the decrease of $[Cl^-]$ as a result of competitive adsorption after the introduction of various extraneous anions, especially corrosion inhibitors, into the standard solutions.[15] This method can be used to investigate the adsorption of not only chloride ions but also of other anions in the presence of which the CIC of the alloy proceeds via the HIE mechanism. In the CIC of high-strength steels, it is possible to investigate by this method, for example, the adsorption of sulphate, phosphate, and other ions and the influence of inhibitors on the latter. For different constructional materials, the research technique is the same, but the exponent in Eqn.(7) varies (see above). The standard conditions (i.e. the material, the electrolyte composition, and the cathodic polarisation potential) are also different in the determination of the critical HIE parameters.

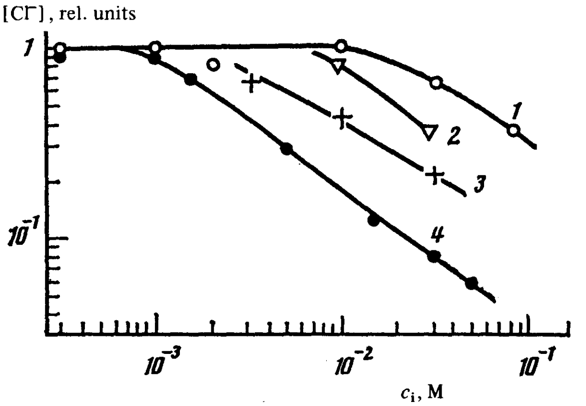

Figure 3. Dependence of the concentration of chloride ions adsorbed on the passivating film at the apex of the crack in the CIC of the steel 33Kh3NMFA in 0.03 M Na_2HPO_4 + 0.01 M NaCl solution on the concentration of inhibitors: *1*) $NaCrO_4$; *2*) hexamethyleneammonium 3,5-dinitrobenzoate (G-4); *3*) $NaNO_3$; *4*) $NaNO_3$; $[Cl^-] = 1$ in solution in the absence of inhibitors; $E_{cp} = -0.8$ V.[15]

Fig.3 presents certain results of a study of the competitive adsorption of chloride ions in the region of the apex of the crack in the presence of inhibitors in the CIC of different materials.[15,19] It shows that the introduction of oxidant anions into the standard solution hinders the adsorption of chloride ions, the nitrate ion, which has come to be regarded as an activator rather than an inhibitor of corrosion, being the most effective. Under the CIC conditions, this anion displaces chloride ions from the surface of the passivating film at the top of the crack much more vigorously than the known general corrosion inhibitors such as chromates, nitrites, and the organic G-4 inhibitor. This influence of nitrate is characteristic of the CIC of not only high-strength steels but also titanium and aluminium alloys.[19]

In this connection, mention should be made of the study[17] in which the CIC of high-strength steel was investigated in distilled water and it was shown that at high rates of growth of the crack nitrates are more effective as CIC inhibitors than nitrites, while chromates do not exhibit an inhibiting activity (at concentrations of 0.01 M). We may also mention a study[16] in which the possibility of the inhibition by nitrate of the corrosion fatigue of the high-strength aluminium alloy 7075 in a solution of chloride was demonstrated. It may be that the adsorption processes in the CIC exhibit a definite specificity which is in fact responsible for the highest adsorption capacity of the nitrate ion and the most effective displacement by the latter of chloride ions from the surface of the passivating film at the apex of the crack. As stated above, this is not associated with either the charges of the anions or with their oxidising capacity.

The above specificity has apparently no direct relation with oxo-ion reduction processes either, because the chromate ion influences the permeability to hydrogen less strongly than nitrate although it is not only reduced on the surface of iron but also enters into the composition of the passivating film in the form of Cr^{3+}.[18] In the CIC of aluminium alloys, the effectiveness of chromate is also greater than that of nitrate, vanadate, and molybdate,[19] although it has been established by electronic X-ray spectroscopy (ESCA) that it also enters into the composition of the film. The specificity of the adsorption processes in CIC affects also the behaviour of phosphate: being a general corrosion inhibitor, it increases the permeability to hydrogen of passivating films at the apex of the crack (Fig.2). The method for the study of adsorption at the apex of the crack examined above makes it possible to discover similar differences in the behaviour of oxo-ions in CIC and general corrosion; however, the formal ideas about the permeability to hydrogen, constituting its basis, proved insufficient to explain the specificity of the adsorption in CIC. The development of a physical model of the permeability to hydrogen is necessary for this purpose.

The competitive adsorption of chloride and nitrate ions in the CIC of steel A in solutions having the composition (0.001–0.01) M NaCl + (0–0.01) M $NaNO_3$ has been investigated in detail,[15] the results being presented in Fig.4. Fig.4*a* shows that an increase in the concentration of chloride ions in solution reduces sharply K_{HIE}, while an increase of the concentration of nitrate ions increases it. The higher the HIE activator (chloride ion) concentration, the higher the concentration of the HIE inhibitor (nitrate ion) inducing an increase of HIE. Under standard conditions, 0.01 M NaCl with $[Cl^-] = 1$, the relative changes in $[Cl^-]_x$ under real experimental conditions accompanying the changes in the chloride and nitrate ions in solution were calculated from the data in Fig.4*a* with the aid of Eqn.(7). The results of the calculations are presented in Fig.4*b* (curves *2*–*6*): evidently in the absence of nitrate ions the degree of adsorption of chloride ions increases in direct proportion to their concentration in solution, i.e. in the experimental concentration range the adsorption saturation on the surface of the passivating film at the top of the crack is not attained (curve *1*).

Assuming, as was done above in the derivation of Eqns. (2) and (7), that the adsorption of chloride and nitrate ions is described by the Langmuir isotherm, it is possible to calculate from curves *2*–*6* in Fig.4*b* the ratio *R* of the adsorption coefficient β of the chloride ions to the adsorption coefficient γ of the nitrate ions. If, following the introduction into the chloride solution at a certain concentration ((Cl^-)) of a definite amount of nitrate ions up to the concentration ((NO_3^-)), the initial concentration of the adsorbed ions $[Cl^-] = 1$ diminishes by a factor m, then it follows from the formal ideas about competitive adsorption[21] that

$$
\begin{aligned}
[Cl^-]_x &= \frac{1}{m} = \frac{\beta(Cl^-)}{1+\beta(Cl^-)+\gamma(NO_3^-)} , \\
[NO_3^-]_x &= 1-\frac{1}{m} = \frac{\gamma(NO_3^-)}{1+\beta(Cl^-)+\gamma(NO_3^-)} , \qquad (8) \\
R &= \beta/\gamma = \frac{(NO_3^-)}{(m-1)(Cl^-)} .
\end{aligned}
$$

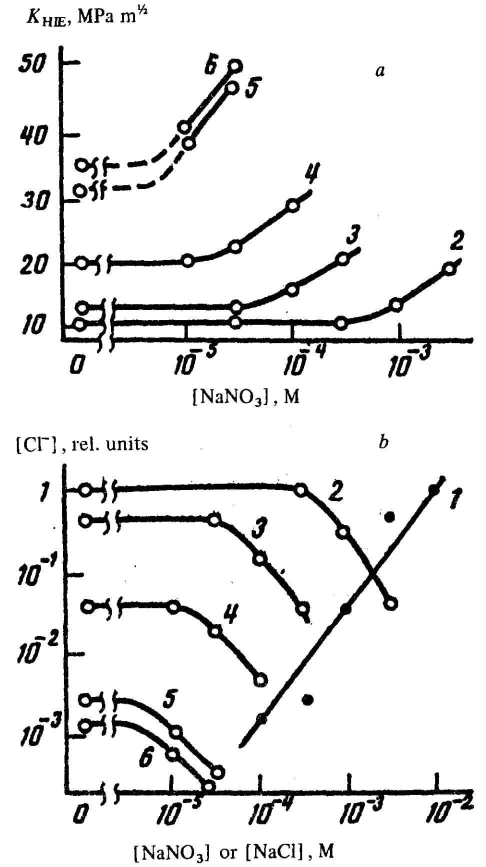

Figure 4. *a*) Dependence of K_{HIE} for the steel 02N18K9M5T on the NaNO₃ concentration in NaCl solutions at different molarities; *2*) 0.01; *3*) 0.003; *4*) 0.001; *5*) 0.0003; *6*) 0.0001; *b*) calculated dependence of the concentration of chloride ions adsorbed on the surface of the film at the apex of the crack on the NaNO₃ concentration in NaCl solutions: *1*) pure NaCl solutions; as in Fig. 4*a* above.[15]

It must be emphasised that, within the framework of the assumptions made, the absolute ratio of the adsorption coefficients of the HIE activators and adsorption is determined from Eqn. (8), although the change in the concentration of the adsorbed HIE activator ions can be determined from Eqn. (7) only in terms of relative units. The following adsorption coefficients of chloride and nitrate ions on the passivating film at the top of the crack in the CIC of steel in neutral solutions have been calculated from the data in Fig. 4*b* by Eqn. (8)[15] (in order of increasing initial NaCl concentrations): 0.06, 0.03, 0.03, 0.03, 0.07, i.e. $R = 0.04 \pm 0.01$. Similar calculations have been made for all the steel–electrolyte systems investigations in the above study;[15] it was established that the strongest inhibitor of HIE in the CIC of steels is the nitrate ion and that the adsorption coefficient ratios depend not only on the nature of the coadsorbed anions but also on the composition of the steel.

The method examined above can be used to investigate the theoretically and practically important question of the dependence of the adsorption of anions on the potential. This question has been examined comprehensively in theoretical electrochemistry but it is far from clear in corrosion theory. The point is that electrochemical studies are carried out on objects which are not corroded in the course of the experiment and which do not form passivating films—on noble metals, mercury, and amalgams. The dependence of the degree of adsorption on the potential under such conditions is determined by the ϕ potential (on a reduced scale), which characterises the charge of the electrode relative to the solution and the structure of the electrical double layer.[22]

Ideas about the adsorption of anions on noble metals are sometimes used in the study of the role of anions in the corrosion processes occurring on real constructional materials. This is apparently insufficiently justified, since no account is taken of the specificity of the interaction of the anions with the passivating films present inevitably on the surface of real alloys in weakly acid, neutral, and alkaline electrolytes on dissolution in the passive and active states and also in pitting, in the growth of cracks in the CIC and HIE, etc. As a rule, the increase of the surface activity of the anions in the sequence $F^- < Cl^- < Br^- < I^-$, observed in adsorption on mercury,[22] is not observed in the corrosion of iron, titanium, and aluminium alloys. For example, the activating capacity of anions in pitting on iron increases in the sequence $F^- < I^- < Br^- < Cl^-$ [23] and anions are adsorbed not only on the passivating film but are also incorporated in the latter.[24] The fluoride ion, which exhibits no surface activity at the mercury–aqueous solution interface, depassivates aluminium alloys most strongly although it does enter into the composition of the film.[25]

There are very few literature data for specific adsorption (especially for the dependence of the degree of adsorption on the potential) on metals of practical importance owing to the lack of a method for the investigation of adsorption in electrolytes *in situ*. The method of adsorption-enhanced Raman scattering (Raman spectroscopy) developed in recent years has been used successfully in the study of adsorption on noble metals.[26] The data obtained by this procedure for iron have been criticised.[27]

As stated above (see Section I), the K_{HIE} for each alloy–electrolyte system depends significantly on the duration and potential of the cathodic polarisation E_{cp} in the determination of K_{HIE} and also on the initial potential E_i at which the passivating layers are formed at the apex of the crack. Therefore, in the determination of the dependence K_{HIE} on the electrolyte composition, these values were constant. The present author[28] investigated the influence of E_{cp} and E_i on the competitive adsorption of anions in the CIC of martensitically ageing steel. The dependence of K_{HIE} on E_{cp} for E_i = const. and the dependence of K_{HIE} on E_i for E_{cp} = const. were determined experimentally for several solutions in which the concentration of the HIE inhibitor ions was varied at a constant concentration of HIE activator ions. Fig.5 shows that an increase of both the concentration of nitrate ions and of the potential E_{cp} increases K_{HIE} (curves *1*–*4*). The influence of the increase of the $NaNO_3$ concentration is caused by the decrease of the adsorption of the HIE activator (the chloride ion) as a result of competitive adsorption and the influence of the increase of E_{cp} is associated with the decrease of the degree of surface coverage by adsorbed hydrogen atoms at the apex of the crack. For each potential E_{cp}, the dependence of the concentration of the chloride ions adsorbed in the region of the apex of the crack (Cl^- on the concentration of nitrate ions in solution was calculated by Eqn.(7); it was shown that E_{cp} in the range from −0.4 to 1.0 V does not affect the adsorption of anions. The decrease of $[Cl^-]$ with increase of $[NO_3^-]$ for different values of E_{cp} is described by the same curve *5* from which the ratio of the adsorption coefficient of chloride and nitrate ions $R = 0.04$, independent of E_{cp}, was determined with the aid of Eqn.(8). An analogous conclusion can be reached on the basis of a study of the adsorption of $[B_4O_7^{2-}]$, namely that R virtually does not change when E_{cp} is varied in the range from −0.2 to −1.0 V for a constant value $E_i = E_{cor}$.

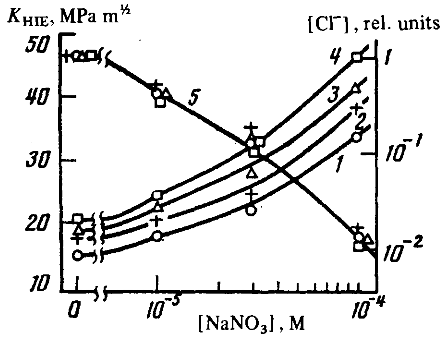

Figure 5. Dependence of K_{HIE} for the steel 02N18K9M5T in 0.0003 M NaCl solution (curves *1*–*4*) and of the concentration of chloride ions adsorbed on the film at the top of the crack (curve *5*) on the $NaNO_3$ concentration in solution at different cathodic polarisation potentials E_{cp} (V): *1*) −0.4; *2*) −0.6; *3*) −0.8; *4*) −1.0.[28]

The dependence of K_{HIE} on the cathodic polarisation potential E_{cp} and the absence of such dependence of R are not in conflict, because different standard values of K_{HIE} for a given E_{cp} for a solution not containing HIE inhibitor ions are used in the calculation of R for different values of E_{cp}. Brief cathodic polarisation does not apparently alter the composition and properties of the passivating film formed at the corrosion potential.

The initial potential E_i, at which the passivating film at the apex of the crack is formed, exerts a significant influence on the competitive adsorption of anions. At the constant potential $E_{cp} = -0.6$ V, the increase of E_i from zero to +0.8 V entails a marked decrease of the degree of adsorption of $B_4O_7^{2-}$ from solutions with identical concentrations of tetraborate and nitrate ions; the ratio of the adsorption coefficients of these anions R diminishes from 0.03 to 0.003.[28] Fig. 6 presents the dependence of R on the potentials E_{cp} and E_i for all the electrolytes investigated in the above study.[28] Evidently, for constant values of E_i, E_{cp} (curves *1* and *2*) hardly influences R, which depends mainly on E_i. This dependence is different for different pairs of competing anions. With increase of E_i, the ratio R for the $B_4O_7^{2-}/NO_3^-$ pair diminishes (curve *3*), that for the pair OH^-/CrO_4^{2-} hardly changes, while that for the pair OH^-/NO_3^- decreases in the range −0.2—+0.4 V and increases with increase of E_i to +0.7 V.

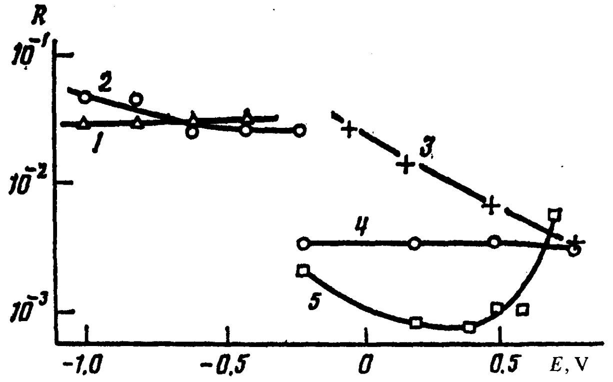

Figure 6. Dependence of the ratio R of the ion adsorption coefficients on E_{cp} (curves *1* and *2*) and E_i (curves *3*–*5*): *1*) Cl^-/NO_3^- pair; *2*) and *3*) $B_4O_7^{2-}/NO_3^-$ pair; *4*) OH^-/CrO_4^{2-} pair; *5*) OH^-/NO_3^- pair.[28]

The method described above makes it possible to calculate the ratio of the adsorption coefficients of two anions when they are present simultaneously in solution but it does not permit the calculation of the absolute adsorption coefficients of individual anions. Nevertheless, the activating or inhibiting capacity of different anions in relation to the HIE process at different potentials E_i in which the passivating film has been formed can be inferred qualitatively from data for the variation of K_{HIE} for the same steel in solutions with different concentrations of such anions. Thus it is seen from Fig.7 that, over the entire experimental range of potentials, the anion $B_4O_7^{2-}$, which does not activate the general and pitting corrosion of steels, increases the permeability of passivating films to hydrogen just as much as the chloride ion—the most active of the halide ions. The joint adsorption of $B_4O_7^{2-}$ and halide ions enhances their activating effect on the HIE process and the differences in the activating effects of different halide ions are virtually abolished. The ability of anions to activate the HIE process at potentials from −0.8 to +0.1 V increases in the sequence $F^- \ll I^- \cong Br^- < Cl^- \cong B_4O_7^{2-}$, while at a potential of +0.5 V it increases in the sequence $F^- \ll I^- \ll Br^- < B_4O_7^{2-} < Cl^-$ (Fig.7, curves *1*–*5*), i.e. halide ions increase the permeability of passivating films to hydrogen in the same sequence in which they activate pitting on iron and which is not the same as the sequence based on the increase of their surface activity and adsorption capacity on mercury.

The following facts are striking. The dependence of the adsorption of different anions on steel on the potential E_i (Figs.6 and 7) exhibits no anomalies at the zero-charge potential of iron (−0.4 V). The anions F^-, SO_4^{2-}, and NO_3^-, which are inactive or weakly active on the mercury–aqueous solution interface, are powerful activators of the corrosion of iron and steels. The adsorption capacity series for halide ions on mercury, which breaks down appreciably in corrosion, pitting, CIC, and HIE of constructional materials in neutral solutions,[15,23] holds in the corrosion of nickel in highly acid solutions at a high rate of dissolution,[29] where passivating films, constituting a separate phase, have apparently not formed on the electrode surface. These facts lead to the conclusion that concepts of the zero-charge potentials of the metals and of the ϕ potentials on the reduced scale (in the form in which they have been formulated in theoretical electrochemistry[22]) are inapplicable to corrosion processes occurring on the surfaces of passivating films. Indeed the zero-charge potential characterises the clean surface of the metal in the absence of specifically adsorbed ions and not the surface with a layer of oxides or hydroxides, which are always formed in the corrosion of technical metals and alloys in weakly acid, neutral, and alkaline solutions.

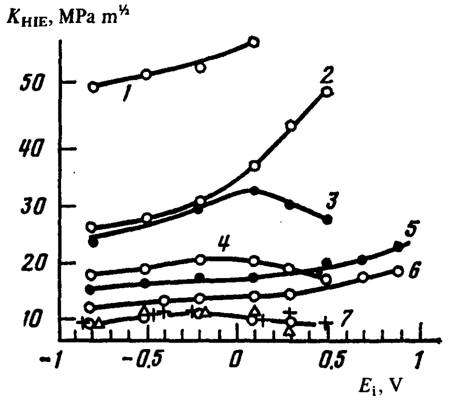

Figure 7. Dependence of K_{HIE} for steel A on the formation potential of the passivating film in solutions of different salts (concentration 0.001 M); *1)* NaF; *2)* NaI; *3)* NaBr; *4)* NaCl; *5)* $Na_2B_4O_7$; *6)* $Na_2B_4O_7$ + NaF; *7)* $Na_2B_4O_7$ + NaCl (or NaBr or NaI); $E_{cp} = -0.8$ V.[28]

Hoar[30] emphasises the disagreement between the zero-charge potentials on clean and oxidised metals in aqueous solutions and suggests that the zero charge potential of the oxidised metal is close to the pitting potential. The concept of the "pH of the zero charge potential (pH_0)* is used in the study of adsorption on oxide and oxidised metallic electrodes. It has been shown that anions are adsorbed on the surfaces of oxides at pH < pH_0 and that their adsorption is independent of the polarisation of the electrode over a wide range of potentials.[31] A tendency to use the concept of pH_0 in corrosion studies has arisen recently. For example, it has been shown[32] that in a chloride solution a decrease of pH_0 of aluminium (pH_0 = 9.1) when the latter is alloyed with molybdenum (pH_0 = 1.95) increases the pitting potential from −0.7 to −0.5 V.

The method for the investigation of adsorption on a passivating film proposed by the present author[15,28] makes it possible to obtain information *in situ* about the adsorption processes at the apex of the crack in the CIC at different potentials and is fairly sensitive (up to 10^{-5} g-ion litre^{-1} for chloride and nitrate ions). It can be used to study any constructional materials in the CIC of which HIE plays an important role. Some of the results of the calculations by this method, for example, data for the adsorption of chloride ions on the surface of a passivating film at the apex of the crack in the CIC of the AL27-1 aluminium alloys have been tested by the ESCA method. It follows from the calculated data that,[19] when $NaNO_3$ is introduced into the 0.5 M CrO_3 + 0.01 M NaCl solution at a concentration of 0.01 M, the concentration of chloride ions adsorbed on the passivating film diminishes by a factor of five. It has been established by the ESCA method that [Cl^-] is 1.5 at.% in the initial solution, while after the introduction of 0.01 M $NaNO_3$ it is not more than 0.5 at.%. This confirms the more general conclusion of the above study that, in the simultaneous presence of chloride and nitrate ions at equal concentrations (in the range 0.01–0.1 M) in 0.5 M CrO_3 solution, the adsorption of chloride ions on the passivating film is almost completely suppressed.

The competitive adsorption of anions in the CIC of the AL27-1 aluminium alloy and the study of adsorption by the ESCA method have been described in detail in studies[19,20] where it was shown, in particular, that the adsorption isotherm of chloride ions, calculated by Eqn.(7), is very close to the experimental isotherm obtained by the ESCA method. Extensive possibilities for experimental tests (by studying the adsorption, saturation with hydrogen, and permeability to hydrogen of thin films, etc.) have arisen as a result of the investigation of high-strength steels because in these materials it is possible to select conditions for the determination of K_{HIE} in the absence of the growth of the crack, i.e. when $K_{HIE} < K_{ISCC}$. The state of the surfaces of the model specimens, investigated, for example, by the ESCA method, is closer to the state of the real surface at the top of the stationary crack than under the conditions of its growth.

IV. THE DEGREE OF SURFACE COVERAGE OF THE PASSIVATING FILM ON A METAL AT THE APEX OF THE CRACK BY ADSORBED HYDROGEN ATOMS

The first two stages in the HIE process (the discharge of hydrogen ions and the adsorption of hydrogen atoms on the surface of the passivating film at the top of the crack until the attainment of a degree of surface coverage θ with subsequent transport of hydrogen through the film to the film–metal interface) are especially important, because each of them may become the rate-limiting stage in the HIE accompanying the CIC under certain conditions. It must be specially emphasised that the degree of such coverage of the film–solution interface by adsorbed hydrogen atoms can significantly exceed the degree of coverage of the nickel–metal interface, because passivating films are barriers to the penetration of hydrogen to the metal both in CIC and in gas-phase HIE, so that the boundary conditions for the diffusion of hydrogen in the metal are determined to a very large extent by the permeability of the film to hydrogen. For example, the presence of 2–3 monolayers of the oxide on the surface of tantalum reduces the rate of adsorption of hydrogen by a factor of 10^{10}.[33] The role of passivating films as barriers to the penetration of hydrogen into the metal is one of the few questions in the theory of CIC for which there is virtually no disagreement (in its qualitative treatment), but in the few studies[12,34,35] which have been devoted to the determination of θ for adsorption on iron, steel, and nickel the role of films is as a rule not considered.

The method for the determination of the degree of surface coverage θ by adsorbed hydrogen atoms of the film at the top of the crack in CIC[36] is based on the quantitative concept of the permeability of passivating films to hydrogen. In the study of the dependence of K_{HIE} and V_{cr} on the cathodic polarisation potential E_{cp} for the same alloy–electrolyte system, the coefficients in Eqns.(2) and (3), namely ξ, α, and β, can be regarded as constant; the dependence is then determined solely by the dependence of θ on the potential. Since the above constant coefficients in Eqns.(2) and (3) are unknown, the determination of the absolute values of θ from the results of corrosion-mechanical tests is impossible. However, having adopted $\theta = 1$ for certain standard conditions (the compositions of the alloy and the electrolyte and the potential E_{cp}), it is possible to determine the relative changes in θ_x as the potential is varied. It follows from Eqns.(2) and (3) that

$$\theta_x = \frac{V_{cr,st}}{V_{cr,x}}\left(\frac{K_{HIE,st}}{K_{HIE,x}}\right)^n . \qquad (9)$$

The standard potential for each alloy–electrolyte system is chosen arbitrarily (as a rule, this is the most negative potential in the series of experiments).

The dependence on the potential E_{cp} on the degree of coverage θ by hydrogen atoms of the surface of the passivating film on the metal at the apex of the crack in the CIC of the high-strength steels N18K9M5T, 40Kh13, and 38N4MFA and the VT20 titanium alloy has been investigated.[36] All the steel specimens and some of the titanium specimens were tested in the state of planar deformation (the exceptions where the thickness of the titanium specimens did not satisfy the formal requirements[14] will be noted below). The relative error in the experimental determination of K_{HIE} was 4%, while the error in the calculation of θ by Eqn.(9) was about 40%.

Fig.8 presents the dependence of the surface coverage by hydrogen atoms of the passivating film at the top of the crack on E_{cp} in the CIC of the steel 02N18K9M5T in different solutions at pH 10. Thus, in view of its high tendency to undergo HIE, this steel is particularly convenient for the investigation of such dependence, since its HIE under CIC conditions in alkaline solutions at $E_{cp} = -(0.2–0.8)$ V can be induced for $K \leq K_{ISCC}$, i.e. in the absence of the growth of cracks at the corrosion potential. This extends the range of the potentials investigated and reduced significantly the scatter of the values of θ, because in the calculation of θ one can disregard the critical rates of growth of the cracks and hence the errors in their measurement. The cathodic polarisation potential $E_{cp} = -0.8$ V was selected as standard for electrolytes. It must be emphasised that the adoption of $\theta = 1$ for standard conditions does not imply the assumption of the complete surface coverage of the film by adsorbed hydrogen, since the method employed does not permit the determination of the absolute values of θ. Presumably the coverage at $E_{cp} = 0.8$ V is close to the maximum, because at more negative potentials (down to −1 V) it hardly changes in all the electrolytes investigated. For the 0.03 M Na_2HPO_4 + 0.1 M NaCl solution (Fig.8, curve *1*), the region of weak dependence of θ on the potential ranges from −0.4 to −0.8 V. For electrolytes without chloride ions and for the solution having the composition 0.03 M Na_2HPO_4 + 0.05 M $NaNO_3$ + 0.1 M NaCl, in which the adsorption of chloride ions is significantly suppressed by nitrate ions, the decrease of θ with the increase of the potential can be described by the general curve *2*, for which $\Delta E/\Delta \lg\theta$ in the range from −0.3 to −0.8 V is 0.25 V. In the solution 0.03 M Na_2HPO_4 + 0.1 M NaCl, the decrease of θ with increase of the potential from −0.8 to −0.4 V is not quite so intense (curve *1*), but in the range from −0.4 to −0.2 V the rate of decrease of θ accelerates and curves *1* and *2* have approximately equal slopes.

A study[34] devoted to the determination of θ by the pulsed anodic polarisation of an iron electrode in the solution 0.0001 M NaOH + 0.1 M Na_2SO_4 (pH 9.5), i.e. under conditions close to those of the present author's study[36] (Fig.8, curve *1*), showed that in the potential range from −0.3 to −0.4 V, the coverage θ varies from 0.05 to 0.12 and $\Delta E/\Delta \lg\theta =$ 0.27 V. For nickel, the main alloying component on the steel 02N18K9M5T in an alkaline solution in the region of low (up to 0.3) coverages, this coefficient is 0.20 V.[35] The similarity of the values of $\Delta E/\Delta \lg\theta$ obtained under the initial conditions by direct electrochemical methods[34,35] to those obtained by the indirect computational method described in the present study can be regarded as evidence for the validity of the assumptions underlying the computational method.

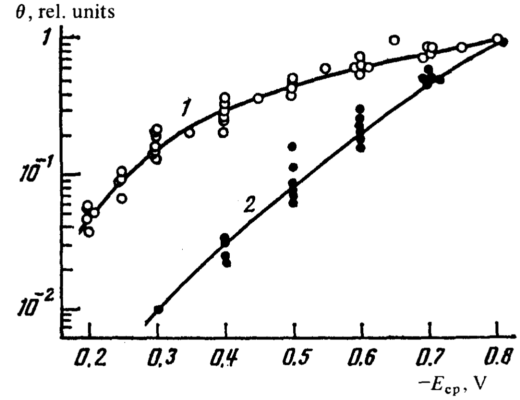

Figure 8. Dependence on the cathodic polarisation potential of the degree of surface coverage by adsorbed hydrogen atoms of the surface of the passivating film at the top of the crack under the conditions of the CIC of the steel 02N18K9M5T in solutions at pH 10: *1*) 0.03 M Na_2HPO_4 + 0.1 M NaCl; *2*) NaOH (or 0.03 M Na_2HPO_4) + 0.05 M $NaNO_3$ + 0.1 M NaCl.[36]

The concept of the permeability to hydrogen of the passivating layers on a metal at the apex of the crack in the CIC and the method for the determination of θ arising from it have no fundamental limitations associated with the nature of the material. They can be used for any alloy–electrolyte system in which there is a possibility of the growth of the crack via the HIE mechanism under CIC conditions and which is characterised by different types of influence of the cathodic polarisation on the growth of cracks, which constitutes the experimental basis for the determination of K_{HIE} and V_{cr}. Only high-strength steels satisfy these conditions in the CIC in the majority of aqueous solutions, but, by a suitable selection of the composition of the electrolyte, it is possible to extend significantly the range of such materials and to include in it austenite stainless high-strength steels and titanium, zirconium, and aluminium alloys (Section I). Their selection consists in seeking the optimum combination of the concentrations and nature of the electrolyte components—passivators and activators. The role of the passivator consists in hindering or fully suppressing the growth of cracks via the local dissolution mechanism, which increases K_{ISCC}, while the role of activators is to ensure the permeability of the passivating layers at the top of the crack to hydrogen sufficient for HIE. It has been established by means of such selection that solutions based on chromium trioxide are universal for the determination of the role of HIE in the CIC of various constructional materials. For example, different types of influence of cathodic polarisation on the growth of cracks in the CIC of high-strength steels and titanium and aluminium alloys can be observed in the solution 1 M CrO_3 + 0.1 M NaCl.[3,15,36]

V. HYDROGEN-INDUCED EMBRITTLEMENT IN CORROSION-INDUCED CRACKING AT POSITIVE POTENTIALS

Studies on HIE (in particular on the dependence of θ on E_{cp}) in solutions based on chromium trioxide are of special interest, because they make it possible to observe HIE at potentials $E_{cp} > 0$ (relative to the n.h.e.). In these solutions, the corrosion potentials of steels and titanium alloys are +(0.5–0.8) V, which permits the determination of K_{HIE} and V_{cr} over a wide range of cathodic polarisation potentials including extremely positive potentials.

It has come to be assumed that at positive potentials HIE is impossible,[37] because the electrochemical evolution of hydrogen is thermodynamically impossible. However, although in the majority of alloy–electrolyte systems HIE under CIC conditions is indeed observed at negative potentials, this view is not uncontroversial. Data have been published on HIE in the CIC of steels[38] and titanium alloys[8] at potentials in the range +(0.1–0.15) V in acid buffer solutions at pH 0–1, i.e. under conditions which rule out the additional acidification of the electrolyte in the crack owing to the hydrolysis of the corrosion products.

The theory of the hydrogen electrode deals with two consecutive electrochemical reactions: the discharge of hydrogen ions and the combination of hydrogen atoms into molecules with liberation of gaseous hydrogen via several possible mechanisms. As a result of the first reaction, absorbed hydrogen atoms capable of penetrating through the passivating layers and ultimately causing HIE, are formed on the electrode surface. This reaction is primary and is therefore most important for the HIE process. On metals which effectively adsorb and absorb hydrogen, it can lead to high surface coverages by hydrogen atoms at fairly high positive potentials (up to +0.4, 0.3, 0.27, and 0.21 V on platinum, palladium, rhodium, and nickel respectively[39]); at the zero charge potential relative to the n.h.e., the degree of surface coverage of these metals in 0.5 M H_2SO_4 solution is close to unity.[39–41] The hydrogen evolution reaction at negative potentials influences the HIE process in CIC insofar as the degree of surface coverage of the passivating film on the metal at the apex of the crack by adsorbed hydrogen atoms depends on the ratio of the rate constants for the discharge and hydrogen evolution reactions.

The hydrogen electrode theory does not take into account the adsorption energy of hydrogen atoms on the electrode surface although there are indications in the literature[40,42] that the overpotential of the hydrogen evolution reaction and the degree of surface coverage depend on the adsorption energy and on the presence of oxide layers on the metal surfaces. For example, the free energies of formation of TiH_2 and TiH are −87 and −63 kJ mol^{-1} respectively, which indicates the thermodynamic feasibility of the formation of the corresponding hydrides (and hence also of the adsorption of hydrogen atoms as the first stage in the hydride formation reaction) at potentials of +0.45 and +0.65 V respectively.[43] The enthalpy of adsorption of hydrogen on the clean iron surface ranges from −52 to −120 kJ mol^{-1} according to various data,[6,9,44] i.e. the formation of adsorbed hydrogen atoms on the iron surface when hydrogen ions are discharged in acid electrolyte is possible at potentials up to +(0.27–0.61) V (without taking into account the overpotential of the discharge reaction and the influence of passivating layers).

In connection with the question of the possibility of HIE at positive potentials under discussion, mention should be made of the increase of the sodium segregation potential in neutral and alkaline solutions on mercury:[45] the reversible sodium segregation potential is −2.71 V, but appreciable reduction of sodium ions with formation of an amalgam begins already at −1.2 V, i.e. at a potential more positive by 1.5 V than the standard value. This phenomenon, induced by the decrease of the free energy of sodium on formation of the amalgam, has apparently the same nature as the discharge of hydrogen ions at positive potentials on platinum, palladium, nickel, and other metals with a high hydrogen adsorption energy.

In the study of HIE in solutions based on chromium trioxide, the compositions and the concentrations of the solution components were selected empirically for each alloy on the basis of the following inter-related requirements:[15,36] (1) the ratio of the concentrations of the activators (NaCl and Na_2SO_4) to the passivator (CrO_3) concentration should be the maximum possible; (2) at the corrosion potential E_{cor} = +(0.5–0.8) V, the alloy must exist in a stable passive state; (3) the current density at the most negative (standard) cathodic polarisation potential should not exceed 0.3 mA cm^{-2}. The fulfilment of all these requirements ensures a high permeability of the passivating layers at the top of the crack to hydrogen, low (or zero) rates of growth of cracks via the LAD mechanism at the corrosion potential and for high values of K, as well as insignificant changes in the electrolyte composition after brief cathodic polarisation. For example, tests on the VT20 titanium alloy were performed in (0.5–2) M CrO_3 + 0.1 M NaCl solutions [pH 1–0, E_{cor} = +(0.75–0.85) V].[36] The dependence of K_{HIE} on E_{cp} was determined and the relative changes in θ were calculated from Eqn.(9). Fig.9 shows that in all electrolytes an increase of the potential from −0.4 to 0 V entails a smooth decrease of θ and then a sharp fall. It is noteworthy that the values of K_{HIE} corresponding to θ > 0.2 were obtained under planar deformation conditions and those corresponding to a lower value of θ were obtained under the conditions of a mixed strained state of the specimen. For this reason, the values of θ in the range 0.01–0.2 in Fig.9 may be somewhat too low.

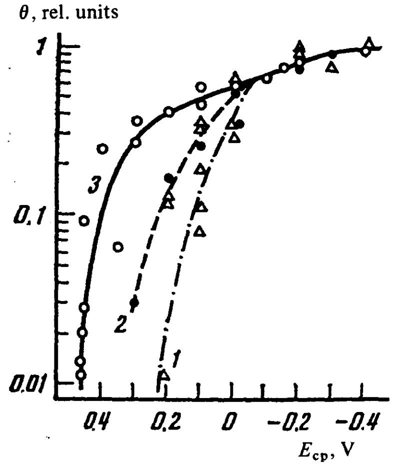

Figure 9. Dependence on the cathodic polarisation potential of the degree of surface coverage by adsorbed hydrogen of the surface of the passivating film at the top of the crack under the conditions of the CIC of the VT-20 titanium alloy in 0.1 M NaCl solutions with different amounts of added CrO_3: *1*) 2 M; *2*) 1 M; *3*) 0.5 M.[36]

In connection with the problem formulated—the investigation of the possibility of HIE at positive potentials—it is more important to emphasise that at potentials up to +0.45 V (see curve *3* in Fig. 9) the degree of surface coverage of the passivating film at the apex of the crack by adsorbed hydrogen atoms exceeds 0.01 and is sufficient to accelerate the growth of the cracks in the CIC of a titanium alloy via the HIE mechanism. The identity of the above potential with the standard potential for the formation of TiH_2 in acid solutions is apparently fortuitous and cannot be regarded as proof of the hydride mechanisms of the HIE of the VT20 alloy.

Compared with titanium, high-strength steels show a much smaller tendency to be passivated in chromium trioxide solutions and the chromate ion reduction reaction on the surface takes place more vigorously, so that the dependence of θ on E_{cp} in the HIE of high-strength steels was investigated in solutions with a lower concentration ratio $NaCl/CrO_3$ than for the VT20 alloy.[36]

Fig. 10 shows that θ falls sharply with increase of E_{cp}; however, at sufficiently positive potentials in the range +(0.1–0.5) V the values of θ are in the range 0.003–0.001 and are sufficient for the growth of cracks via the HIE mechanism. The possibility of determining such low values of θ by the method proposed by the present author[36] indicates its high sensitivity, which greatly exceeds the sensitivity of the known electrochemical methods. This is because in HIE of high-strength steels—materials showing the greatest tendency towards HIE for which the degree of surface coverage by hydrogen atoms ($\theta \cong 0.0001$) exceeds by several orders of magnitude the permeability to hydrogen—was used as the indicator of the presence of adsorbed hydrogen at the apex of the crack. Evidently the sensitivity of the metal should increase with increase of the strength of the steel (i.e. with increase of its tendency towards HIE) and as the values of K in the determination of θ approach K_{IC}.

In the above study[36] no account was taken of the possibility of a change in the pH of the electrolyte in the crack owing to hydrolytic processes and of the incomplete external cathodic polarisation at the top of the crack; as a result of the above processes, the true pH and the potential E_{cp} at the apex of the crack may be other than on the surfaces of the specimen. It is therefore necessary to emphasise that the titanium alloy and high-strength steels existed in the solutions of chromium trioxide in a stable passive state (i.e. the dissolution and hence the hydrolytic processes involving the dissolution products were virtually completely suppressed) and also that, at E_{cp} = +(0.2–0.5) V, the external polarisation current density did not exceed 10 μA cm^{-2}. The latter implies that, under the conditions of high electrical conductivity of the solution (pH 0) and the maximum opening of the crack at high $K \cong 0.9\ K_{IC}$, such currents could induce only a slight ohmic potential drop in the crack and the true potential at the apex of the crack should be more positive than the value of E_{cp} specified by the external cathodic polarisation.

The data in Figs. (9) and (10) can be regarded as experimental proof of the HIE of titanium alloys and high-strength steels at potentials significantly greater than zero relative to the n.h.e., i.e. under conditions where the electrochemical evolution of hydrogen is thermodynamically impossible, but, as shown above, one cannot rule out the possibility of the discharge of hydrogen ions and the formation of adsorbed hydrogen atoms on the surface of the passivating film.

The results described above justify the consideration of the discharge of hydrogen ions (without subsequent evolution of hydrogen) as a possible cathodic depolarisation process together with oxygen and hydrogen depolarisation processes. Judging from the high rates of growth of cracks in the HIE during CIC, the discharge of hydrogen ions may occur at a high rate over a wide range of potentials, including high positive potentials, but the adsorption nature of this process limits its depolarising capacity: for the maximum surface coverage (one hydrogen atom per metal atom), the amount of electricity consumed in the discharge process should not exceed 160–200 μC cm^{-2}) depending on the lattice constant of the metal. This implies that, in the usual corrosion processes, the discharge of hydrogen ions ceases rapidly and does not play an appreciable role as the cathodic depolarisation process, but in corrosion with constant renewal of the surface it can become an important cathodic process. It was shown above that, despite the low coverages θ at positive potentials, the discharge of hydrogen ions is in fact responsible for the growth of cracks via the HIE mechanism in CIC. In corrosion fatigue, corrosion wear, and rapid anodic dissolution, for example, under electrochemical polishing conditions or in chemical milling, the discharge of hydrogen ions (without the evolution of hydrogen) can play a significant role and can lead to the saturation of the metal with hydrogen.

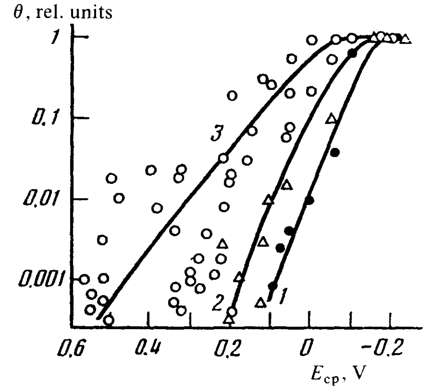

Figure 10. Dependence on the cathodic polarisation potential of the degree of surface coverage by hydrogen atoms of the surface of the passivating film at the top of the crack under the conditions of the CIC of the steels 4Kh13 (curve *1*) and 02N18K9M5T (curve *2*) in the 2 M CrO_3 + 0.1 M Na_2SO_4 + 0.003 M NaCl solution and of the steel 38N4MFA (curve *3*) in the 2 M CrO_3 + 0.02 M Na_2SO_4 solution.[36]

The role of the discharge of the hydrogen ions as the main cathodic process is apparently greatest on the freshly formed surfaces of the metal after a short (80–100 μs) time of their exposure to electrolytes. The study of corrosion and electrochemical properties of the freshly formed surfaces shows that, for many metals (iron, aluminium, titanium, etc.), the corrosion potential increases immediately after the cut and then sharply diminishes after 80–150 μs to values close to the standard potentials of the corresponding metals.[46] For lifetimes in the range 80–150 μs, the corrosion potential of the freshly formed surfaces in neutral solutions is as a rule more positive by 0.1–0.3 V than the hydrogen evolution potential and the current density of the anodic and cathodic processes reach several hundreds of mA cm^{-2}. It has been noted[46] that the nature of such an intense cathodic process is obscure because, owing to fusion-dependent limitations, this process cannot involve the reduction of the dissolved oxygen and the electrochemical evolution of hydrogen is thermodynamically impossible. Under these conditions, the discharge of hydrogen ions at positive potentials is the most likely cathodic process. It must be emphasised that, despite these limitations associated with its adsorption nature, this process can ensure the experimentally observed cathodic current densities (up to 1 A cm^{-2}) during periods up to 200 μs. In all cases the rate of the cathodic process on the freshly formed surfaces fell sharply owing to the formation of the primary passive film after brief exposures.[46]

The adsorption nature of the cathodic discharge of hydrogen ions makes it possible to account for certain characteristic features of the CIC and HIE of constructional materials in chromium trioxide solutions. These solutions, having the composition (0.5–2) M CrO_3 + (0.01–0.1) M NaCl, possess specific properties promoting the elucidation of the role of HIE in the CIC of different constructional materials. For example, only in this medium is it possible to observe HIE in the CIC of aluminium alloys,[3] while in the CIC of titanium alloys and high-strength steels in CrO_3 + NaCl solutions, K_{HIE} is much lower than in the presence of other oxidants.[36] As a rule, at sufficiently high cathodic polarisation potentials $K_{HIE} < K_{ISCC}$, i.e. passivating layers are formed in chromium trioxide solutions in the CIC at the top of the crack. These layers effectively suppress the growth of cracks via the LAD mechanism and at the same time exhibit a fairly high permeability to hydrogen.

In contrast to other oxo-ions, chromates are reduced on the surfaces of metals, as a result of which Cr^{3+} ions enter into the composition of the passivating film.[18] Studies by the ESCA method have shown[20] that the concentration of Cr^{3+} ions on the surface of the passivating film on the AL27-1 alloy in 0.5 M CrO_3 + 0.01 M NaCl solution is 5–6 at.%. It is known[3] that hydrogen is hardly adsorbed on aluminium oxides and hydroxides. It is also known[47] that the heat of adsorption of hydrogen on chromium oxide is very high. Presumably the Cr^{3+} ions entering into the composition of the passivating layers from aqueous chromate solutions generate effective adsorption centres on which hydrogen ions are discharged. Thus the passivating films in chromium trioxide solutions, which retain effective protecting properties and suppress CIC via the LAD mechanism, can promote the penetration of hydrogen into the metal and can facilitate CIC via the HIE mechanism.

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In conclusion one should note that the quantitative concept of the permeability to hydrogen of passivating layers on a metal at the apex of the crack in the CIC of constructional materials, considered in the present review, is based on several postulates each of which separately does not conflict with known facts but cannot be fully justified theoretically or experimentally. Nevertheless, on the basis of this concept, it has been possible to reach *a priori* certain definite conclusions which have been confirmed experimentally.[10,13,15] This can be regarded as proof of the validity of the initial postulates of the concept considered and the method, arising from it, for the investigation *in situ* of the adsorption of activator ions on the passivating film at the apex of the crack in CIC, the method for the investigation of competitive adsorption, and the method for the determination of the dependence of the relative changes in the degree of surface coverage by the hydrogen adsorbed on the film on the cathodic polarisation potential. The above methods were used in the study of a wide range of processes which are of theoretical and practical importance (the development of physical ideas about the mechanism of HIE, the study of the strained state of the material at the apex of the crack, the study of inhibitors of corrosion, CIC, and HIE, the search for solutions for hydrotests, etc.).

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Activation and Catalytic Reactions of Alkanes in Solutions of Metal Complexes

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The reactions of saturated hydrocarbons and compounds modelling them with metal complexes, leading to the cleavage of the C-H and C-C bonds, are examined. In particular, processes which result in the formation of organometallic derivatives are described and the mechanism of the oxidation of alkanes by enzymes and their chemical models is discussed.
The bibliography includes 355 references.

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I. INTRODUCTION

The relatively low reactivity of saturated hydrocarbons is due to the absence of π and n electrons from their molecules and the low polarity of the C–H and C–C σ-bonds. At the same time, since paraffinic hydrocarbons (the store of which, especially methane, in nature is still large) are one of the types of chemical organic raw materials, the problem of their conversion into functional derivatives (alcohols, ketones, and acids) and also of the synthesis of olefins and aromatic hydrocarbons from alkanes is currently of very great importance. The hydrocracking and isomerisation reactions of paraffins, which make it possible to obtain valuable forms of motor fuel, are also of considerable practical importance. The main industrial processes in which alkanes are used as raw materials occur at high temperatures (above 150–200 °C), frequently in the presence of heterogeneous catalysts (for example, dehydrogenation, aromatisation, the reaction of methane with water which affords the CO + H_2 mixture, the cracking of methane to acetylene and hydrogen, nitration, fluorination by CoF_3, etc.). The radical-chain processes (photochemical chlorination by Cl_2, oxidation by molecular oxygen initiated by light or radicals, sulphochlorination, etc.), which are carried out at low temperatures, constitute a special field. However, the selectivity of these reactions is low and complex mixtures of products are usually formed. Finally, the ability of certain micro-organisms and higher animal cells to oxidise alkanes by oxygen at the usual temperature has long been known. Biological oxidation is usually selective. For example, certain micro-organisms oxidise only the terminal methyl group of hydrocarbons, converting it initially into an alcohol (ω-hydroxylation).

New homogeneous reactions of alkanes, occurring in solution or in the gas phase, have been discovered recently.[1] Thus the reactions of saturated hydrocarbons with electrophiles in solutions of strong acids or superacids have been discovered.[1,2] The proton, the attack of which on the alkane gives the alkonium ion $C_nH_{2n+3}^+$, which subsequently decomposes with cleavage of the C–H and C–C bonds, functions as the electrophilic species in solutions of the acids FSO_3H–SbF_5 or HF–SbF_5. The electrophilic substitution of hydrogen in alkanes by the nitro-group takes place under the influence of $NO_2^+PF_6^-$ in dichloromethane at room temperature, while the reaction of an alkane with Cl_2 in SbF_2–SO_2ClF takes place even at −78 °C. Solutions of fluoranil in HF–HF–SbF_5 oxidise methane, propane, and n-pentane.[3] The dissolution of H_2O_2 or O_3 in FSO_3H–SbF_5–SO_2ClF generates respectively the $H_3O_2^+$ and HO_3^+ species, which attack alkane molecules electrophilically resulting in the formation of various oxygen-containing derivatives. Like ozone, iodoxybenzene $PhIO_2$ oxidises aromatic alkyl-substituted hydrocarbons.[4] In reactions with electrophiles, the reactivity of the bonds in branched alkanes usually diminishes in the sequence 3° > C–C > 2° > 1° (where 1°, 2°, and 3° denote respectively the primary, secondary, and tertiary C–H bonds). In the reaction with $H_3O_2^+$, the reactivity varies in the sequence[2] 3° > 2° > 1° > C–C. An analogous behaviour has been observed also in the interaction of branched alkanes with radical and carbene species.[1] Thus hydroxylation of alkanes by peracids (for example, trifluoroperacetic)[1,5] also proceeds with the "normal" selectivity 3° > 2° > 1°, while the reaction with *cis*- or *trans*-1,2-dimethylcyclohexane proceeds with complete retention of the configuration. The reaction takes place via the "oxenoid" mechanism—with insertion of the oxygen atom in the C–H bond without the formation of intermediate free-radical or ionic species. Thus in all the reactions enumerated the reactants interacting with alkanes are to some extent electrophilic. The reaction of an alkane (methane, ethane, propane) with the phenylium ion $C_6H_5^+$ in the gas phase has been described recently.[6] The product of the insertion of the phenylium cation in the R–H bond of the alkane, resembling the familiar Wheland complex, which is converted into C_6H_5R after transferring H^+ to a base, is formed as an intermediate. The interaction of 1,10-B_{10}.$H_8(N_2)$ with a mixture of CO and CH_4 leads to the formation of $MeB_{10}H_7(CO)_2$ and $Me_2B_{10}H_6(CO)_2$, but the reaction mechanism has not been established.[7]

The first reaction of an alkane with a metal complex in which an organometallic compound, i.e. a derivative containing a metal–carbon bond,[9] is formed as an intermediate was discovered[8] in 1969. This reaction is responsible for the H–D exchange in methane, ethane, and higher alkanes in the C_nH_{2n+2}–D_2O–$PtCl_4^{2-}$ system. The ability of alkanes to be oxidised in the C_nH_{2n+2}–H_2O–$PtCl_4^{2-}$–$PtCl_6^{2-}$ system, also with the intermediate formation of organometallic σ-complex of platinum, was discovered somewhat later.[10] The characteristic features and mechanisms of these reactions have been studied in detail. Section II of the present review review is devoted to such reactions. New reactions in which the alkane molecule is activated in solution with a transition metal complex were discovered subsequently. The number of such reactions continues to increase and an increasing number of laboratories in various countries are becoming involved in the study of this rapidly developing field. Section III presents a survey of studies on this field carried out during the last decade. Major advances have been achieved recently in the understanding of the mechanism of the biological oxidation of alkanes. The studies on the chemical models of enzymes catalysing the oxidation of alkanes are developing vigorously. It is becoming clear that the active centres interacting with the C–H bond in the alkane include high-valence derivatives of a metal (usually iron). Reactions involving the direct oxidation of alkanes by high-valence metal compounds have been known for many years.[11,12] Section IV deals with the enzymic oxidation of alkanes and the oxidation of the latter by high-valence metal complexes, associated with the enzymic process. The review covers studies published mainly in the 1980's; earlier investigations were described in detail in other reviews.[13–18]

II. REACTIONS OF ALKANES WITH PLATINUM(II) AND PLATINUM(IV) COMPLEXES

The closest analogue of the activation of alkanes involving the dissociation of weakly polar strong C–H or C–C bonds is the activation of the H_2 molecule. Indeed the H_2 and CH_4 molecules exhibit a definite similarity, because they contain only σ-bonds (H–H or C–H), which have virtually identical homolytic dissociation energies $D(R{-}H)$ = 103–104 kcal mol^{-1} and are characterised by a high ionisation potential and a low electron affinity. At the end of the 1960's considerable advances were made in the solution of the problem of the activation of H_2 by metal complexes (see, for example, James[19]). The key stage of such activation is the oxidative addition of hydrogen in accordance with the scheme

$$M^n + H_2 \rightarrow H{-}M^{n+2}{-}H$$

On the basis of the similarity of the properties of H_2 and alkanes, it might have been supposed that the latter are also capable of being activated by metal complexes undergoing the oxidative addition reaction with the latter. As already mentioned, the first such system is represented by the platinum(II) chloride complex.[8] It was subsequently found that the platinum(IV) complex is capable of oxidising alkanes. Analogous reactions are known also for aromatic compounds.

1. Characteristic Features and Kinetics of the Reactions

(a) Deuterium Exchange in the Presence of Platinum(II) Complexes

When methane or another alkane is heated to ~100 °C in a sealed tube containing a solution of $PtCl_4^{2-}$ in the D_2O–CD_3COOD mixture, the hydrogen atoms in the alkane are replaced by deuterium.[1,8,13–17] The process also occurs in water but in the presence of acetic acid the rate of reaction increases by a factor of 30 (when account is taken of the solubility of alkanes in CH_3COOH). The reaction is of first order with respect to the hydrocarbon. The rate constant k for the deuterium exchange involving cyclohexane in the presence of various platinum(II) complexes decreases in the following sequence for $[C_6H_{12}]$ = 0.15 M, $[HClO_4]$ = 0.1 M, [Pt(II)] = 0.02 M, and 100 °C: K_2PtCl_4 (2.78), $K_2Pt(NO_2)Cl_3$ (0.366), $KPt(NH_3)Cl_3$ (0.777), $KPt(DMSO)Cl_3$ (0.056), $KPt.(py)Cl_3$ (0.025). The values of 10^3k (litre mol^{-1} s^{-1}) are given in brackets. When the anions X^- are added to the system, new complexes catalysing the H–D exchange in cyclohexane are formed via the reaction

$$S_2PtCl_2 + 2X^- \rightleftarrows X_2PtCl_2^{2-} + 2S\,.$$

The following rate constants for this reaction have been obtained (10^3k, litre mol^{-1} s^{-1}):[13] 6.30 (in the absence of X^-); 6.28 (in the presence of CF_3COO^-); 6.26 (F^-); 6.06 (SO_4^{2-}); 4.10 (Cl^-); 2.47 (Br^-); 0.394 (I^-); 0.115 (NO_2^-); 0.106 (CN^-). Ultimately this led to the establishment of the sequence based on the influence of the ligands in the platinum(II) complex on the rate of H–D exchange:[13]

$$PPh_3 \simeq py < DMSO < CN^- < NO_2^- < NH_3 < I^- < Br^- < Cl^- < F^- \simeq H_2O\,. \quad (1)$$

This sequence is the opposite to that based on the *trans*-effect of the corresponding ligands. The rate constants for the H–D exchange reaction catalysed by platinum(II) are described satisfactorily by the two-parameter equation

$$\lg(k/k_0) = \rho^*\sigma^* + n\psi\,, \quad (2)$$

where σ* is the Taft constant taking into account the polar influence, ψ the parameter characterising the conjugation of the substituent in the α-position relative to the H atom with the radical reaction centre, and n the number of substituents. The value ρ* = −1.4 indicates weak electron-accepting properties of the platinum(II) complex, while the presence of the resonance term may indicate that the C–H bond is dissociated homolytically. A linear correlation has also been observed between the logarithm of the rate of H–D exchange in hydrocarbons and their ionisation potentials.[13]

Unbranched alkanes are the most reactive in the H–D exchange reaction. On the other hand, in the exchange of branched hydrocarbons the "reverse" reactivity sequence is observed, i.e. 1° > 2° > 3°. Evidently this is associated with the strong influence of steric factors. The low rate of exchange in the methyl and methylene groups adjoining the t-butyl group in 2,2-dimethylpropane and 2,2-dimethylbutane can be explained in the same way. A characteristic feature of the reaction is multiple exchange—the alkane molecule can exchange several H atoms for D without leaving the coordination sphere of the metal complex. The multiple exchange parameter M for different alkanes varies in the range 1.4–1.7 and increases only slightly with decrease of the reaction temperature.

(b) Oxidation by Platinum(IV) Complexes

When a solution of H_2PtCl_6 and Na_2PtCl_4 in H_2O (or in aqueous CF_3COOH) is heated in the presence of alkanes (100–120 °C, 0.25–5 h), a mixture of isomeric alkyl chlorides, alcohols, trifluoroacetates, and ketones is formed, while platinum(IV) is reduced to platinum(II).[1,10,13–17] The kinetics of the reaction with participation of methane have been described in detail.[20] When cyclic alkanes (cyclohexane and decalin) are oxidised, aromatic hydrocarbons (benzene, naphthalene) are obtained. The π-complex of hex-1-ene with platinum(II) has been isolated[21] in 1% yield from the mixture of products formed in the reaction of H_2PtCl_6 with hexane in the CF_3COOH–H_2O mixture. Acetic acid is oxidised by a mixture of Pt(IV) + Pt(II) chloride complexes to chloroacetic acid. The reaction of $PtCl_6^{2-}$ with saturated hydrocarbons is catalysed by added $PtCl_4^{2-}$. In the absence of such additives, an induction period is observed, its duration decreasing with increase of the amount of added $PtCl_4^{2-}$. In the presence of heteropoly-acids, the platinum(II) formed in the reaction can be reoxidised by air and the oxidation of CH_4 to CH_3Cl (CH_3OH is then also oxidised) becomes catalytic.[22] Another catalytic system for the chlorination of alkanes contains K_2PtCl_4, H_2PtCl_6, and $HgSO_4$ immobilised on silica gel.[23]

As in deuterium exchange, the dependence of the rate of oxidation of alkanes (with a constant k_n) in the $PtCl_6^{2-}$ + $[PtCl_{4-n}(H_2O)_n]^{n-2}$ system passes through a maximum with increase of n (at $n = 2$), but in the case of isobutane $k_2 =$ 3.8 litre mol^{-1} s^{-1} differs insignificantly from k_3 and espepecially from k_1 (1.9 and 3.7 litre mol^{-1} s^{-1} respectively). The complexes with $n = 0$ and 4 are almost inactive in the reaction.[1] When the H–D exchange and oxidation reactions of cyclohexane in CF_3COOH catalysed by Pt(II) + Pt(IV) were compared, the following features were discovered:[24] the sum of the rates of the oxidation and H–D exchange reactions is independent of the concentrations of CF_3COOH and Pt(IV), but with increase of [Pt(IV)] keeping $[CF_3COOH] =$ const., the rate of oxidation rises, while with increase of $[CF_3COOH]$ for [Pt(IV)] = const. the rate of H–D exchange increases. These data show that the two processes have a common initial stage.

The oxidation reaction of alkanes containing between 1 and 4 carbon atoms in an aqueous medium is of first order with respect to the hydrocarbon and has a fractional order (0.77) with respect to platinum(II).[14] The activation energy (~20 kcal mol^{-1}) for the oxidation reactions of ethane, propane, or butane is approximately equal to the activation energy for the H–D exchange involving ethane (18.6 kcal mol^{-1}). The chlorination of acetic acid proved to be most convenient for kinetic study. The order of this reaction is unity with respect to platinum(II) and CH_3COOH. At low concentrations of the added Cl^- ions the rate of reaction is proportional to $[Cl^-]_{add}^{-1}$ while at high concentrations it is proportional to $[Cl^-]_{add}^{-2}$. The order of the reaction with respect to platinum(IV) varies from 0 to 1. The role of steric factors is strongly manifested in the reaction involving the oxidation of alkanes by the $PtCl_6^{2-}$ + $PtCl_4^{2-}$ system.[1,25] As for the system with $[H_2PtCl_6] = 0.02$ and $[K_2PtCl_4] =$ 0.05 M in water at 98 °C the oxidation rate constants diminish on passing from normal to branched hydrocarbons; for n-butane and 2-methylpropane, they are respectively 11.5 and 8.2 s^{-1}, for n-pentane, 2-methylbutane, and 2,2-dimethylpropane they are 15.3, 11.2, and 1.0 s^{-1}, and for n-octane and 2,2,4-trimethylpentane the corresponding values are 15.4 and 3.6 s^{-1}. In the series of normal alkanes, the oxidation rate constant increases with increase of the number of carbon atoms atoms: methane (1.6) < ethane (6.6) < propane (9.9). For C_5–C_8 n-hydrocarbons, k is approximately the same (~16 s^{-1}). The latter factor can be accounted for if it is assumed that the chlorine atom substitutes mainly the hydrogen atoms in the 1- and 2-positions in the chain on oxidation by the Pt(IV) + Pt(II) system. In general the number of active (capable of substituting their hydrogen atoms by Cl) carbon atoms n_a in the alkane C_nH_{2n+2} is defined by the formula[25] $n_a = n - n_{tert} - 5n_{quat}$, where n_{tert} and n_{quat} are the numbers of ternary and quaternary carbon atoms in the molecule respectively.

It has been found recently that, when a solution of H_2PtCl_6 and n-hexane in CH_3COOH is irradiated by light (λ > 300 nm) or γ-quanta, a π-complex of hex-1-ene with platinum(II), isolated in the form of the pyridine adduct $[CH_3(CH_2)_3.CH{=}CH_2]PtCl_2py$, is formed.[26-29] The yield of the π-complex in the γ-induced reaction reaches 17%. The photochemical reaction is of first order with respect to hexane.

2. Intermediate Organometallic Compounds

In earlier studies[1,13-17] it was postulated on the basis of the investigation of the kinetics of the reactions of alkanes with platinum complexes, and certain indirect evidence, that the interaction of alkanes with both platinum(II) and platinum(IV) leads to the intermediate formation of alkyl π-complexes of platinum. In recent years new indirect and direct evidence has been obtained for the involvement of these complexes in the process.

(a) The Stages in the H–D Exchange and Oxidation Reactions

The H–D exchange and oxidation reactions apparently begin with the attack by the reactive form of the platinum(II) complex on RH, which results in the formation of an alkylplatinum(II) σ-complex:

$$PtCl_4^{2-} \rightleftarrows PtCl_3^- + Cl^- \ , \qquad (3)$$

$$PtCl_3^- \rightleftarrows PtCl_2 + Cl^- \ , \qquad (4)$$

$$PtCl_2 + RH \rightleftarrows RPtCl + H^+ + Cl^- \ . \qquad (5)$$

In the absence of platinum(IV), the alkyl σ-derivative undergoes electrophilic attack by the D^+ ion (for the cleavage of the M–C bond by electrophiles—see, for example, Kochi[30]):

$$RPtCl + D^+ + Cl^- \rightarrow RD + PtCl_2 \ . \qquad (6)$$

On the other hand, if a platinum(IV) derivative is present in the system, it interacts with the platinum(II) σ-complex and converts it into an alkylplatinum(IV) σ-complex. The latter reacts with the nucleophile X (H_2O or Cl^-) and affords ROH or RCl:

$$RPt\,(II) + Pt\,(IV) \rightarrow RPt\,(IV) + Pt\,(II) \ , \qquad (7)$$

$$RPt\,(IV) + X^- \rightarrow RX + Pt\,(II) \ . \qquad (8)$$

At a temperature above 100 °C and a low platinum(IV) concentration the rate of reaction depends on [Pt(IV)] and on the acidity of the medium and stage (7) is apparently rate-limiting. The activation energy for this stage is low (~9 kcal mol^{-1}). At a temperature below 100 °C and for a low platinum(IV) concentration, the rate of the entire reaction is determined by the rate of stage (5). The activation energy for the reaction under the given conditions (~20 kcal mol^{-1} for C_2–C_4 alkanes) is naturally close to that for H–D exchange (18.6 kcal mol^{-1} for ethane).[14] Since the platinum(II) complex, used for the initial activation of RH, returns to the system in stage (7), the alkane oxidation reaction is catalytic with respect to platinum(II) and the platinum(IV) acts as an oxidant.

Evidence for the formation of intermediates or organometallic compounds in this process is presented below.

(b) Isolation of Aryl σ-Complexes and Their Properties

It is well known that transition metal complexes, in particular platinum complexes, are capable of cleaving the C–H bond intramolecularly with formation of cyclometallated compounds.[31,32] Compounds containing both sp^2-hybridised carbon atoms (aromatic rings) and groups with sp^3-hybridised carbon atoms (CH_2 and CH_3) are capable of entering into the cyclometallation reaction.[33-37] Calculation has shown[14] that the intramolecular metallation of the C–H bond should be 10^3–10^6 times faster than the intermolecular reaction.

In order to confirm the possibility of the formation of complexes with a C–Pt(IV) σ-bond in intermolecular reactions with $PtCl_6^{2-}$, use was made of aromatic compounds, since it was known that the reaction with benzene and other arenes gives rise to oxidation products (especially chlorobenzene) analogous to the alkane oxidation products and that aryl σ-complexes should be much more stable than the alkyl σ-complexes. It was found that heating of a solution of H_2PtCl_6 and an aromatic compound ArH in the CF_3COOH–H_2O mixture or in CH_3COOH leads to the formation of fairly stable aryl σ-complexes of platinum(IV) in yields up to 95%, which can be isolated in the form of anionic adducts with ammonia after chromatography on silica gel containing NH_3:[38–42]

$$ArH + PtCl_6^{2-} \xrightarrow[\text{2) } SiO_2 \cdot NH_3]{\text{1) } CF_3COOH-H_2O} [\sigma\text{-}ArPtCl_4NH_3]\,NH_4 \quad . \tag{9}$$

Complexes of naphthalene and *o*-nitrotoluene have been characterised by X-ray diffraction[38,43] and ^{195}Pt NMR spectra have been obtained for a number of complexes.[44] The kinetics of the accumulation of the complexes and of their decomposition, leading to the formation of ArAr, ArCl, and platinum(II), have been investigated.[42,45–48] The accumulation of the aryl σ-complex is accompanied by its *para–meta* isomerisation: if in the initial instant the substitution takes place mainly (to the extent of ~90%) in the *para*-position in toluene, then the statistical distribution $m:p = 2:1$ is gradually attained. The substituent does not enter the *ortho*-position for steric reasons. It has been established by the method of competing reactions[42,49] that the relative rates of reactions with participation of C_6H_5X decrease in the following sequence of X: OH (16), OCH_3 (8.5), CH_3 (3), C_2H_5 (2.7), OC_6H_5 (2.0), $CH(CH_3)_2$ (1.9), H (1.0), C_6H_5 (0.9), F (0.3), $COCH_3$ (0.1), COOH (0.09), Cl (0.08), NO_2 (0.04). The logarithms of these quantities are correlated with the Hammett constant σ and the Brown constant σ^+ (with the parameters $\rho = -3.0$ and $\rho^+ = -1.5$). On the basis of the data obtained, a mechanism has been proposed[42] for the reaction—electrophilic substitution in the aromatic ring.[48] In terms of its behaviour in the arene metallation reaction and also as regards the behaviour of the aryl σ-complexes formed in relation to nucleophiles (arenes, olefins),[50–53] platinum(IV) resembles palladium(II).[54] The gold(III) chloride complex apparently metallates arenes also via the electrophilic substitution mechanism.[55] Arenes interact with Na_2PtCl_4 on heating with a solution in $CF_3COOH-H_2O$ or CH_3COOH.[56] This apparently entails the formation of aryl σ-complexes of platinum(II) which are comparatively unstable but can be converted by treatment with H_2PtCl_6 into aryl σ-complexes of platinum(IV). Thus the platinum(II) chloride complex apparently behaves as an electrophile in the reaction with arenes. On the other hand, the reaction of arylplatinum(II) σ-complexes with $PtCl_6^{2-}$ can be regarded as a model of stage (7) in the oxidation of alkanes.

Reaction (9) can be induced not only by heating but also by light[26,28,48,57] or γ-irradiation.[27] The arenes C_6H_5X form the following series in terms of substituents X based on the variation of the relative rate of the photochemical reaction with $PtCl_6^{2-}$:[26] OH (8), OC_2H_5 (4.1), OCH_3 (4.0), OC_6H_5 (1.9), CH_3 (1.0). The logarithms of these quantities are correlated with the constants σ_n^+ ($\rho^+ = -1.5$). It has been suggested[48] that the radiation-induced reactions begin with electron transfer from the arene to platinum(IV) and then the Wheland complex is formed, as in the case of a thermal reaction.

All the reactions of arenes considered here apparently proceed by the electrophilic substitution mechanism postulating the delocalisation of the positive charge of the arene ring in the Wheland complex formed as an intermediate. Since such delocalisation is impossible for fully saturated hydrocarbons, the reaction with arene must be regarded merely as confirmation of the possibility of the formation of compounds with an M–C bond when alkanes are activated; on the other hand, the mechanisms of the interaction of the metal complexes with a C–H bond in alkanes and arenes should differ.

(c) Alkane σ-Complexes

The reactions involving the oxidative addition of alkyl halides to transition metal complexes containing phosphine or amine ligands, resulting in the formation of a compound with M–C bonds, are well known.[9,58] However, it has been found only recently[59] that the chloride complex $PtCl_4^{2-}$, not containing "stabilising" ligands, combines with CH_3I at room temperature in aqueous solution to form a methyl σ-complex of platinum(IV). An interesting feature of the reaction is that the sixth coordination site in the octahedral molecule of the product is occupied by water, while the I^- ion is bound to another molecule of the platinum(II) complex (PtI_2 is formed and precipitates). The reaction with C_2H_5I [60,61] and CH_3COCH_2I [62] proceeds analogously:

$$RI + PtCl_4^{2-} \xrightarrow{H_2O} RPtCl_4(H_2O)^- + I^- \quad . \tag{10}$$

In the presence of an excess of I^- ions at 80 °C, RI is converted rapidly and quantitatively into the alkane, the platinum(II) complex functioning as the catalyst:[63]

$$RI + I^- + H^+ \xrightarrow{Pt^{II}} RH + I_2 \quad . \tag{11}$$

The methyl σ-complex formed in reaction (10) ($R = CH_3$) eliminates CH_3Cl with formation of a platinum(II) complex:

$$CH_3PtCl_5^{2-} \rightarrow CH_3Cl + PtCl_4^{2-} \quad ; \tag{12}$$

$$CH_3PtCl_4(H_2O)^- + Cl^- \rightarrow CH_3Cl + PtCl_4^{2-} + H_2O \quad . \tag{13}$$

It has been concluded[64] on the basis of the kinetic parameters of the decomposition of the methylplatinum(IV) σ-complex that the steady-state concentration of this complex, formed in the reaction of CH_4 with the Pt(II) + Pt(IV) system at a methane pressure of 1.01×10^7 Pa, [Pt(II)] = 0.1 M, and 120 °C, should not exceed 10^{-6} M in aqueous solution. However, owing to the increase of the concentration of CH_4 and the higher rate of its reaction with platinum(II) in the $CF_3COOH-H_2O$ solution, this value may be higher by 1–2 orders of magnitude.

Similar alkyl σ-complexes of platinum(IV) can be obtained in the reaction of $PtCl_6^{2-}$ with certain alkyl derivatives of non-transition metals. Thus $PtCl_6^{2-}$ reacts slowly[65] with $(CH_3)_4Sn$ in CD_3COOD at room temperature with formation of $CH_3PtCl_5^{2-}$. The reaction is accelerated by the addition of $PtCl_4^{2-}$ and is of first order with respect to platinum(II):

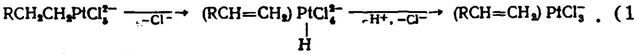
$$(CH_3)_4Sn + PtCl_6^{2-} \xrightarrow{PtCl_4^{2-}} CH_3PtCl_5^{2-} + (CH_3)_3SnCl \quad . \tag{14}$$

In the absence of $PtCl_6^{2-}$, tetramethyltin reacts with Na_2PtCl_4 in aqueous acetone, also forming a methylplatinum(IV) σ-complex. The precipitation of metallic platinum is then observed. The reaction partly proceeds as oxidative addition of the components involved in the Me_3Sn-Me bond to platinum(II). As in the case of RI [reaction (10)], one component adds to the platinum(II) atom, while the other is bound by another platinum(II) species (reducing the latter):

$$(CH_3)_4Sn + 2PtCl_4^{2-} + H_2O \rightarrow CH_3PtCl_4(H_2O)^- + Pt + (CH_3)_3SnCl + 3Cl^- . \tag{15}$$

The reaction involving the transfer of the methyl group from methylcobalamine to platinum(IV) is likewise catalysed by a platinum(II) complex.[66] It is noteworthy that reaction (14) to a certain extent models the interaction of the Pt(IV) + Pt(II) system with saturated hydrocarbons. Reaction (15) probably also has features in common with the reaction of alkanes with the platinum(II) complex. The cleavage of the $Sn-CH_3$ bond by the $PtCl_6^{2-}$ complex is accelerated by light.[65] The formation of the complex $C_2H_5PtCl_5^{2-}$ (in addition to $CH_3.$ $.PtCl_5^{2-}$) has been observed by ^1H NMR in the photochemical reaction of $PtCl_6^{2-}$ with $(CH_3)_2Sn(C_2H_5)_2$ in CD_3COOD. Light apparently accelerates the conversion of the ethyl σ-complex into the ethylenic π-complex.

Thus the reactions in which there is a possibility of the formation of platinum(IV) derivatives and alkyl fragments containing a hydrogen atom in the β-position, mainly the photoinduced reactions of the ethyl derivatives of tin and germanium with $PtCl_6^{2-}$, oxidative addition of ethyl iodide or n-hexyl iodide to $PtCl_4^{2-}$, and thermal or photochemical reactions of hexane with $PtCl_6^{2-}$, lead to olefinic π-complexes of platinum(II). The most probable mechanism of the conversion of alkyl σ-complexes into olefinic π-complexes involves the β-elimination of hydrogen with reduction of platinum(IV) to platinum(II):



$$\mathrm{RCH_2CH_2PtCl_5^{2-}} \xrightarrow[-\mathrm{Cl}^-]{} \mathrm{(RCH{=}CH_2)}\underset{\displaystyle \mathrm{H}}{\mathrm{PtCl_4^{2-}}} \xrightarrow[-\mathrm{H}^+,\,-\mathrm{Cl}^-]{} \mathrm{(RCH{=}CH_2)PtCl_3^-}\,. \qquad (16)$$

The formation of the methyl σ-complex of platinum(IV) in the reaction of CH_4 with the Pt(II) + Pt(IV) system in H_2O has been demonstrated directly.[20] It was found that treatment of the reaction mixture, after the removal of methane from the latter, with sodium tetrahydroborate leads to the evolution of CH_4, formed on reduction of the complex $CH_3 . PtCl_5^{2-}$. The kinetic curve corresponding to the concentration of the methyl σ-complex determined in this way has a maximum corresponding to the same reaction time as the points of inflection on the kinetic curves for the consumption of $PtCl_6^{2-}$ or the accumulation of the final products (CH_3OH and CH_3Cl). The activation energy for the decomposition of the methyl σ-complex is 26 ± 2 kcal mol^{-1}, the decomposition rate constant at 120 °C is $0.14\ s^{-1}$, and the maximum concentration of the complex is 7.7×10^{-5} M. Hence it is possible to calculate the rate of decomposition of the complex at its maximum concentration (1.1×10^{-5} mol $litre^{-1}\ s^{-1}$), which is close to the maximum rate of consumption of platinum(IV) or accumulation of the product (1.0×10^{-5} mol $litre^{-1}\ s^{-1}$). Finally the σ-complex formed in the reaction with methane was characterised by the ^1H NMR spectrum, which proved to be identical with the spectrum of the complex obtained in reaction (10).

III. REACTIONS WITH COMPOUNDS OF OTHER METALS

As early as 1969, it was reported that the complex $H_3Co . (PPh_3)_3$ catalyses the H–D exchange between methane and D_2 in benzene solution.[8] Other hydride or low-valence metal complexes, inducing the H–D exchange in aromatic and aliphatic hydrocarbons, have been discovered in recent years. For example, processes of this kind have been described for the naphthalene–C_6D_6–$ReH_5(PMe_2Ph)_2$ [67] and H_2–C_6D_6–$ReH_7[P(C_6H_{11})_3]_2$ systems.[68] In solution in C_6D_6 the isopropyl or cyclohexyl groups R in the complexes $RuH_4 . (PR_3)_3$ are involved in the H–D exchange.[69] The photolysis of a solution of toluene or ethylbenzene in C_6D_6 in the presence of $CpMoH_3(Me_2PCH_2CH_2PMe_2)$ (Cp = cyclopentadienyl) leads to the substitution of H by D both in the aromatic ring and in the alkyl chain.[70] Under the influence of light, H–D exchange has been observed between $IrH_3(CO)(Ph_2PCH_2 . CH_2PPh_2)$ and C_6D_6.[71] The exchange between alkanes and D_2 is catalysed by the allyl hydride complex of rhodium immobilised on silica gel.[72,73] All the reactions enumerated apparently include the stage involving oxidative addition to the metal complex and in certain cases can begin with the elimination of H_2 from the hydride derivative.

In the presence of $TiCl_4$, Cp_2TiCl_2, or VCl_4, dimethylaluminium chloride exchanges the hydrogen atoms of the methyl group for deuterium atoms from CD_4.[74,75] CH_2D_2 is formed preferentially, CH_3D and CD_3H being produced in addition. The proposed reaction mechanism includes the reversible disproportionation of the methyl groups linked to the transition metal atom M, which leads to the formation of a carbenium complex, the latter combining in its turn with deuteriomethane. The electronic structures of the complexes H_nMCH_3 and H_mMCH_2 (M = Ti, V, or Cr) have been calculated by the LCAO-MO SCF method.[76] It was found that the capacity of these compounds for the formation of the carbenium complex ($MCH_3 \rightarrow MCH_2 + H_2$) varies in the sequence Ti < V < Cr.

Under the influence of Cp_2V, methane exchanges the hydrogen atoms for deuterium atoms from D_2 (the overall yield of CH_3D, CH_2D_2, CHD_3, and CD_4 is 2–6% after 24 h in the presence of 35% of methane and at a pressure of 250 mmHg; the product ratios are 1.0 : 0.2 : 0.3 : 0.12).[74,77,78] Benzene used as the solvent also enters into the H–D exchange reaction. The process mechanism includes the following stages:

$$\begin{gathered} M + CH_4 \rightleftarrows H{-}M{-}CH_3\,, \\ H{-}M{-}CH_3 + D_2 \rightleftarrows D{-}M{-}CH_3 \rightleftarrows H{-}M{-}CH_2D\,, \\ H{-}M{-}CH_3 + D_2 \rightleftarrows H{-}M{-}D + CH_3D\,, \\ M + D_2 \rightleftarrows D{-}M{-}D\,, \\ D{-}M{-}D + CH_4 \rightleftarrows D{-}M{-}H + CH_3D\,. \end{gathered} \qquad (17)$$

It is of interest that the H–D exchange between CD_4 and C_6H_6 under the influence of Cp_2V is strongly accelerated in the presence of ethylene, which may be associated with the fact that the addition of methane to the ethylene complex via the mechanism

$$M(\pi\text{-}CH_2{=}CH_2) + CD_4 \rightleftarrows CD_3{-}M{-}CH_2CH_2D \qquad (18)$$

is dynamically more favourable than the addition involving the formation of an alkyl hydride complex. In the CD_4–C_2H_4–C_6H_6 system the ethylene molecule plays the role of agent transferring deuterium from methane to benzene.

Iridium(III) and rhodium(III) chlorides catalyse the H–D exchange with the solvent (CH_3COOD–D_2O) in arenes and alkanes.[1,13–15,79] As for the platinum(II) complexes, multiple exchange is observed, arenes react faster than alkanes, and the exchange does not occur in the *ortho*-position in substituted arenes. Finally we may note that the interaction of alkanes with metal atoms or ions M (see, for example, Refs.80–87) leads to the cleavage of the C–H and C–C bonds and the formation of M–H and M–C bonds.

(a) Isolation of Alkyl Hydride Complexes

In certain cases the alkyl hydride complexes formed on oxidative addition (accompanied by the dissociation of a C–H bond) of arenes, alkyl groups linked to aromatic rings, and even alkanes are fairly stable and can be isolated. For example, on heating or photolysis, the complexes Cp_2WH_2, Cp_2WCO, and Cp_2WHCH_3 give rise to a coordination-unsaturated tungstocene species Cp_2W, which readily combines with aromatic or aromatic alkyl-substituted hydrocarbons.[88] For example, in the reaction with toluene the products are $Cp_2 . W(H)C_6H_4CH_3$ and $Cp_2W(CH_2Ph)C_6H_4CH_3$, i.e. tungsten is inserted both in a C–H bond in the aromatic ring and in a bond involving an sp^3-hybridised carbon atom. The thermal reaction of Cp_2W with mesitylene affords $Cp_2W(H)CH_2C_6H_3 . (CH_3)_2$. However, cyclohexane and neopentane do not give rise to insertion products in this instance. The oxidative addition of alkanes with formation of alkyl hydride complexes was first demonstrated directly in studies using iridium complexes. Thus the iridium dihydride derivative $Cp'Ir(H)_2 . PMe_3$ (Cp′ = pentamethylcyclopentadienyl) produces, after irradiation in solution in cyclohexane or neopentane, the complexes $Cp'(PMe_3)Ir(H)(C_6H_{11})$ and $Cp'(PMe_3)Ir(H) . CH_2C(CH_3)_3$ in a satisfactory yield.[89–91] Other saturated hydrocarbons and benzene also readily add to an iridium complex. The alkyl hydride complexes obtained have been characterised by ^1H and ^{13}C NMR and infrared spectra. By treatment with $CHBr_3$ at −60 °C, these complexes were converted into the more stable derivatives $Cp'(PMe_3)Ir(Br)R$. Irradiation of $Cp'Ir(H)_2PMe_3$ in the $C(CH_3)_4$ + C_6D_{12} mixture led to the formation of $Cp'(PMe_3)Ir(H)CH_2C(CH_3)_3$ and $Cp'.(PMe_3)Ir(D)C_6D_{11}$ with very small admixtures of cross-addition products. Thus both components involved in the R−H bond add to the same metal atom. The reaction of alkanes with the complex $Cp'Rh(H)_2PMe_3$ takes place analogously under irradiation conditions at a temperature below −30 °C.[89,92,93] It is of interest that the cyclopropyl hydride complex rearranges to the rhodacyclobutane derivative.[94] The relative rates of the reactions with various hydrocarbons have been determined by the method of competing reactions[89,92] (Table 1). The selectivity (both substrate and positional selectivity) proved to be much higher for the rhodium complex than in the case where an iridium complex was used. When the cyclohexyliridium hydride complex (I) or the n-pentyliridium hydride derivative (II) was heated for 50 h at 140 °C in a mixture of 91.5% of cyclohexane and 8.5% of n-pentane, the following equilibrium was established:

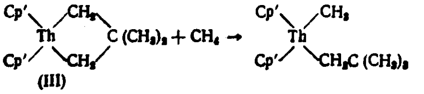
$$\underset{(I)}{Cp'(PMe_3)Ir(H)C_6H_{11}} + CH_3(CH_2)_3CH_3 \overset{K}{\rightleftarrows} \underset{(II)}{Cp'(PMe_3)Ir(H)(CH_2)_4CH_3} + C_6H_{12} \quad (19)$$

and the ratio (II):(I) was 1.0 ± 0.1. Hence the constant $K = [(II)][C_6H_{12}]/[(I)][n\text{-}C_5H_{12}] = 10.6$, which corresponds to $\Delta G^\circ = -2.0$ kcal mol^{-1}. It has been suggested that the entropy changes in the reaction are small and, assuming that the CH_2 and CH_3 bond energies in cyclohexane and n-pentane are 94.5 and 98 kcal mol^{-1} respectively, we find that the energy of the M−C bond in the complex (II) is higher by 5.5 kcal mol^{-1} than in the complex (I).[95] It follows from the estimates that the methyliridium hydride complex $Cp'.(PMe_3)Ir(H)CH_3$ should also be thermodynamically very stable. It was obtained in 58% yield on heating (at 140 to 150 °C) a solution of the complex (I) in cyclo-octane in the presence of methane (20 atm).[89,95]

Table 1. The relative rates of reaction of the complex $Cp'M(H)_2PMe_3$ with hydrocarbons via a C−H bond (irradiation at −60 °C).[89,92]

Hydrocarbon	Relative rate		Hydrocarbon	Relative rate	
	M=Rh	M=Ir		M=Rh	M=Ir
Benzene	19.5	3.9	Ethane	2.0	—
Cyclopropane	10.4	2.1	Cyclopentane	1.8	1.1
Hexane (1°)	5.9	2.7	Neopentane	—	1.14
Hexane (2°)	0.1	0.2	Cyclohexane	1.0	1.0
2-Methylpropane	3.6	—	Cyclodecane	—	0.23
Propane (1°)	2.6	1.5	Cycloheptane	0.14	—
Propane (2°)	0.1	0.3	Cyclo-octane	0.06	0.09
Ethylene	2.4	—			

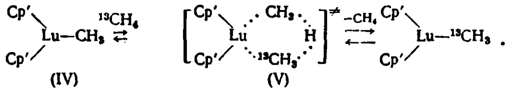
Irradiation of the solution of the carbonyl complex $Cp'Ir(CO)_2$ in perfluorohexane at room temperature in a CH_4 atmosphere (10 atm) led to the formation of $Cp'Ir(CO)(H)CH_3$ in 20% yield.[96] The study of the kinetics of the reaction of the complex $Cp'Rh(H)_2PMe_3$ with arenes and alkanes led to the conclusion that in the case of arenes the oxidative addition is preceded by the coordination of the aromatic hydrocarbons via one of the double bonds and that the $Rh-C_6H_5$ bond is more stable by approximately 13 kcal mol^{-1} than the $Rh-CH_3$ bond.[97] In reaction (20) of the cyclic derivative of thorium(III) with methane (60 °C, in cyclohexane) the methyl group is bound to the metal and hydrogen adds to the ligand carbon atom:[98]



(III)

(20)

This is confirmed by the fact that the reaction with CD_4 (which is 6 times slower than that with CH_4) leads to the formation of a deuteriated complex, evolving neopentane-d_1 after hydrolysis. The exchange reaction (21) of methane with a lutetium complex[99,100] apparently proceeds via a similar mechanism. It has been suggested that reaction (21) takes place via the transition state (V):



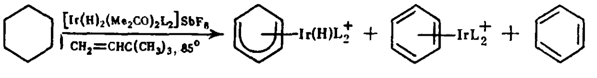
(IV) (V)

(21)

Since lutetium in the complex (IV) is in the +3 oxidation state, it is unlikely that the exchange with $^{13}CH_4$ takes place via the usual oxidative addition, since the latter should result in the formation of the alkyl-lutetium hydride complex (V). In the mechanism involving the transition state (V), the metal atom has electrophilic properties. The rhodium complex immobilised on silica gel, which reacts with methane, is also an electrophile.[101] The reaction proceeds via two pathways, one of which leads to a methylrhodium(III) hydride derivative. When the methylrhodium hydride complex is treated with chlorine, CH_3Cl is formed.

(b) Dehydrogenation of Alkanes

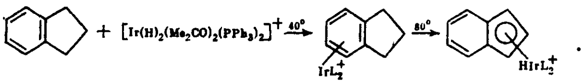
As already mentioned, platinum chloride complexes dehydrogenate alkanes. The complexes of certain metals in a low oxidation state can also abstract hydrogen from aliphatic substituents in phosphine ligands or alkanes. For example, the reaction of $[(cyclo\text{-}octene)_2MCl]_2$ (M = Rh or Ir) with tricyclohexylphosphine in boiling toluene leads to the formation of the derivative $[P(C_6H_{11})_3]M[P(C_6H_9)(C_6H_{11})_2]Cl$, in which the M atom is π-coordinated to the double bond in the cyclohexene group C_6H_9.[102] The cycloalkanes are dehydrogenated in the presence of 3,3-dimethylbutene by the cationic iridium complexes $[Ir(H)_2(Me_2CH)_2L_2]SbF_6$, where $L = PPh_3$ or $(p\text{-}FC_6H_4)_3P$.[103,104] The complex $[CpIr(H)L_2]SbF_6$ is formed from cyclopentane in 82% yield. Cyclohexane affords the mixture of the products (VI) and (VII) as well as benzene in yields of 5, 45, and 32% respectively:



$L = (p\text{-}FC_6H_4)_3P.$ (VI) (VII)

(22)

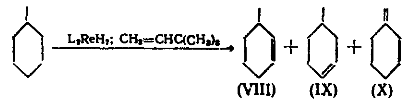
The reaction with cyclo-octane leads to the formation of $[Ir(COD)L_2]SbF_5$, where COD = 1,5-cyclo-octadiene and $L = (p\text{-}FC_6H_4)_3P$, in 75% yield. However, in the presence of 1,8-di(dimethylamino)naphthalene as the base, the process becomes catalytic (8 cycles) and its product is cyclo-octene. Iridium compounds with arenes ArH give rise to complexes which dehydrogenate cyclopentane with formation of a Cp derivative of iridium and the liberation of the free arene.[105] The indan dehydrogenation process is accompanied by an intramolecular rearrangement:[105]



(23)

All the reactions with cationic iridium complexes take place under homogeneous conditions. To demonstrate this, a special test was developed using dibenzo[*a*, *e*]cyclo-octatetrane, which makes it possible to detect the formation of a heterogeneous catalyst from the soluble complex.[106] It has been suggested that the dehydrogenation by the cationic complex includes the oxidative addition to the alkane via a C–H bond to the iridium atom with subsequent dehydrogenation.[103]

The dehydrogenation of alkanes has been studied in detail in relation to reactions with rhenium polyhydride complexes. Thus heating of a solution of L_2ReH_7 ($L = PAr_3$, where Ar = p-FC_6H_4, C_6H_5, or p-$CH_3C_6H_4$) in cycloalkane in the presence of 3,3-dimethylbutene leads to the formation of the complex $CpRe(H)_2L_2$ in the case of cyclopentane[107] or of cycloalkenes in the case of cyclohexane, cycloheptane, and cyclo-octane.[108] When low concentrations of the heptahydride and 3,3-dimethylbutene are used, the dehydrogenation reaction of the alkanes C_nH_{2n} (n = 6, 7, 8) becomes catalytic in relation to rhenium hydride (up to 9 cycles).[109] Under these conditions, methylcyclohexane produces a mixture of three olefins (no other products, for example benzene, have been detected):



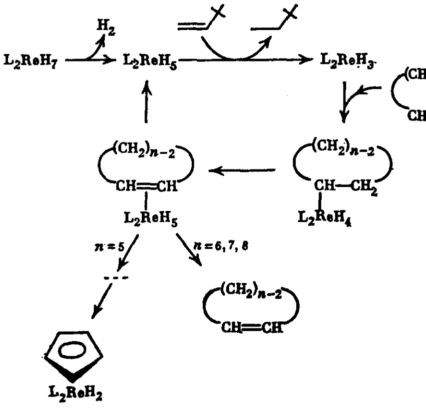
(24)

The ratio of the isomers (VIII), (IX), and (X) depends on the nature of the ligand L (Table 2).[109] The selectivity series $CH_3 > CH_2 > CH$ has been observed in the reaction, but for steric reasons the reagent does not attack the most shielded hydrogen atom (in CH_3 and 2- and 6-CH_2). In the case of the less bulky ligand Et_3P, the content of compound (X) increases at the expense of compound (IX). The proposed process mechanism (Scheme 1) includes the first stage involving the elimination of H_2 followed by the oxidative addition of RH to L_2ReH_3 and the β-elimination of the hydrogen atom with formation of an olefinic π-complex:

Table 2. The ratio of the isomers (in %) formed in reaction (24) as a function of the nature of the ligand L.[109]

L	(VIII)	(IX)	(X)
$(p\text{-}FC_6H_4)_3P$	29	65	6
Ph_3P	28	63	9
Et_3P	27	45	28

Scheme 1

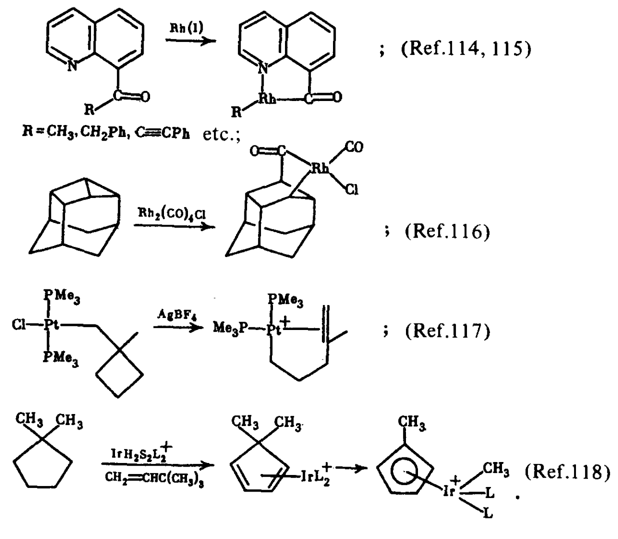


The reaction of $(PPh_3)_3ReH_7$ with n-alkanes leads to the formation of the diene complexes $(RCH=CH-CH=CH_2)Re\cdot(PPh_3)H_3$, which, on treatment with $(MeO)_3P$, give rise to alk-1-enes in yields of more than 95% and a selectivity in excess of 98%.[110] The polyhydrides of other metals, in particular, $(iso\text{-}Pr_3P)_2IrH_5$, $[(p\text{-}FC_6H_4)_3P]_2IrH_5$, and $[(p\text{-}FC_6H_4)_3P]_3RuH_4$ dehydrogenate catalytically (45 to 70 cycles) cyclo-octane to cyclo-octene in the presence of 3,3-dimethylbutene at 150 °C.[111] The dehydrogenation reaction can occur also under the influence of metal atoms. For example, the condensation of tungsten with cyclopentane and PMe_3 gives a 10% yield of $CpW(PMe_3)H_5$,[112] while the interaction of tungsten atoms with cyclohexane and PMe_3 affords the complex $C_6H_6W(H)_2(PMe_3)_2$.[113]

(c) The Cleavage of the C–C Bond

Compared with the C–H bond, the bond between carbon atoms in saturated fragments of alkane molecules is much more resistant to the action of metal complexes. Only reactions involving the opening of the cyclopropane ring and the insertion of Rh in the C–CO bond or bonds in saturated but strained cyclic hydrocarbons are known.[9] Certain examples of such reactions are presented in Scheme 2.

Scheme 2



An instance of the cleavage of a C–C bond in an alkane by metal complexes is known: when octane was heated at 180 °C for 15 h in an atmosphere of H_2 (50 atm) in the presence of $Re_2(CO)_{10}$ + $Al(C_2H_5)_3$, the hydrocarbon was hydrogenolysed with 48% conversion.[119] There are data showing that, in the presence of $Co_2(CO)_8$, the fragmentation of alkanes by γ-radiation is retarded and at the same time the complexes $Co_3(CO)_9CR$, where R = CH_3, C_2H_5, or $CH(CH_3)_2$, are formed.[120]

(d) The Hydroalkylation of Multiple Bonds by Alkanes

Like hydrogen (hydrogenolysis), methane can rupture a metal–alkyl bond (alkanolysis):

$$M-R+CH_4 \rightarrow M-CH_3+RH\ . \qquad (25)$$

The first examples of such reactions was the formation of ethane in the interaction of methane with organoaluminium compounds in the presence of $TiCl_4$, Cp_2TiCl_2, VCl_4, and other complexes.[74,75,121]

As already stated, the possibility of such processes was then demonstrated in the reaction of methane with lutetium and thorium complexes [reactions (20) and (21)]. Taking into account the occurrence of reaction (25), on the one hand, and knowing the mechanism of the multiple bond hydrogenation reaction, on the other, it is reasonable to postulate[74,121,122] the possibility of the addition of R–H to the multiple bond (hydroalkylation):

$$\begin{gathered} M + R{-}H \rightleftarrows H{-}M{-}R\ , \\ H{-}M{-}R + CH_2{=}CH_2 \rightleftarrows CH_3CH_2{-}M{-}R \rightarrow M + CH_3CH_2R\ , \\ CH_3CH_2{-}M{-}R + RH \rightarrow M{-}R + CH_3CH_2R\ . \end{gathered} \tag{26}$$

Indeed, in the reaction of methane with ethylene ($CH_4/C_2H_4 >$ 10, 20 °C, 10 h), propane is formed under the influence of the catalyst $Ti(OC_4H_9)_4 + Al(C_2H_5)_3$ in benzene in a yield of about 20% relative to ethylene.[122] Methane adds to acetylene with formation of propene when acted upon by $Al(C_2H_5)_3$ and and $Fe(acac)_3$ [74,121] or nickel stearate, naphthenate, and naphthenehydroxamate deposited on the surface of nickel hydroxide.[123]

IV. CHEMICAL MODELS OF THE BIOLOGICAL OXIDATION OF ALKANES

1. Enzymic Oxidation

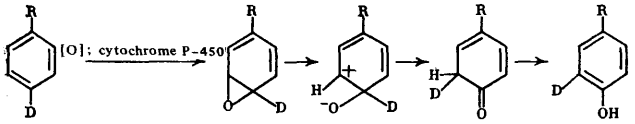
It is well known that various organic compounds, including alkanes, can be oxidised by oxygen in the cells of bacteria, insects, fish, warm-blooded animals, and man as well as higher plants. The group of enzymes catalysing the hydroxylation of CH-containing compounds by oxygen, namely oxygenases, can induce the insertion of only one oxygen atom from O_2 in the C–H bond, while the second oxygen atom is reduced with formation of water:

$$C{-}H + O_2 + AH_2 \rightarrow C{-}OH + H_2O + A\ . \tag{27}$$

In this case the enzymes are referred to as monoxygenases.[124–129] The hydrogen donors AH_2 are NADH, NADPH, the ascorbate anion, and other biological reductants. Certain monooxygenases contain cytochrome P-450—a protein which contains haem as the prosthetic group.[124–134]

(a) Oxidation with Participation of Cytochrome P-450

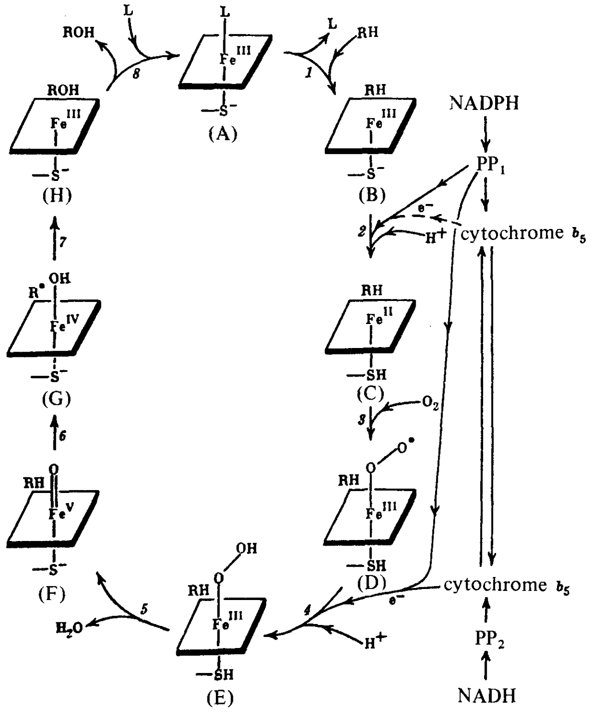
The oxidation of organic substrates by oxygen has been investigated in greatest detail in the liver cell microsomes of warm-blooded animals and also by bacterial monoxygenases containing cytochrome P-450. For example, the monoxygenases of the bacterium *Pseudomonas putida* hydroxylate camphor, while the monoxygenases from the mitochrondria and microsomes in the adrenal cortex cause the side chain of cholesterol to be split off with subsequent hydroxylation of the saturated C–H bonds. It is important that, in the presence of liver microsomes, alkanes and aliphatic acids are hydroxylated predominantly at the terminal (ω) carbon atom. The C–H bonds at the neighbouring (ω − 1) carbon atom of the aliphatic chain are much less reactive. Thus the oxidation of decanoic acid results in the formation of 92% of 10-hydroxydecanoic and 8% of 9-hydroxydecanoic acid. Since the oxidation in the ω- and (ω − 1)-positions is inhibited by carbon monoxide to different extents, presumably the C–H bond activation processes in these positions are catalysed by different monoxygenases. The isotope effect discovered in the hydroxylation of [11-D_2]lauric acid amounts to 3.6. On the other hand, monoxygenases are known (for example those isolated from rat liver microsomes) which hydroxylate alkanes with the "usual" selectivity (thus 1° : 2° : 3° = 1 : 15.4 : 113 for isopentane). A characteristic feature of the oxidation in the presence of monoxygenases is the retention of the configuration of the substrate. The hydroxylation of aromatic compounds proceeds as electrophilic substitution (the ratio $o:m:p$ = 59 : 13 : 28 for toluene) and is accompanied by the so called NIH shift. This phenomenon, consisting in the transfer of a hydrogen (deuterium) atom to a neighbouring position relative to that at which hydroxylation takes place, may be accounted for by the following scheme:



(28)

The oxidation of organic compounds RH by oxygen in the presence of cytochrome P-450 includes at least 8 stages (Scheme 3).[124] The following notation has been adopted in the scheme: PP_1 = NADPH-cytochrome P-450 reductase, PP_2 = NADH-cytochrome b_5 reductase, and S = cysteine residue.

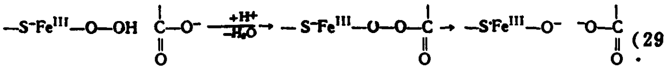
Scheme 3



The formation of the complex (B) in the first stage converts cytochrome P-450 from the low-spin form into the high-spin form. Reduction takes place in the second stage of the process, after which an O_2 molecule is coordinated to the Fe(II) atom. X-Ray diffraction analysis of the complex of myoglobin with O_2 showed that oxygen is coordinated in such a way that the molecular axis of O_2 forms an angle of 120° with the plane of the porphyrin ring [Pauling's structure (D)]. The fourth and fifth stages terminate with the reduction of the complex and the elimination of a water molecule. This results in the formation of the oxenoid (F), whose structure can be represented by several formulae:

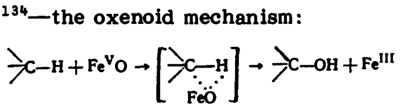
$$-S^{-}Fe^{V}O^{2-} \leftrightarrow -S^{-}Fe^{IV}O^{-} \leftrightarrow -S^{-}Fe^{III}O \leftrightarrow -S^{\cdot}Fe^{III}O^{-}\ .$$

The thiol ligand S^- behaves in this instance as an electron donor. The carboxy-group of one of the aminoacids of cytochrome P-450 and the intermediate acyl peroxide participate in the cleavage of the O–O bond:[124]



$$-S^-Fe^{III}-O-OH\quad -C(=O)-O^- \xrightarrow[-H_2O]{+H^+} -S^-Fe^{III}-O-O-C(=O)- \rightarrow -S^-Fe^{III}-O^-\quad {}^-O-C(=O)- \qquad (29)$$

The sixth stage consists in the rupture of a C–H bond in the substrate molecule. Two alternative mechanisms have been proposed[124,125,134]—the oxenoid mechanism:



$$>C-H + Fe^{V}O \rightarrow \left[>C-H \cdots FeO\right] \rightarrow >C-OH + Fe^{III} \qquad (30)$$

and the radical mechanism with subsequent recombination in the cage:

$$>C-H + OFe^{V} \rightarrow \left[>C^{\cdot}\ HOFe^{IV}\right] \rightarrow >C-OH + Fe^{III}\,. \qquad (31)$$

It may be that the real mechanism of the elementary process includes two stages, the first of which is close to the H atom abstraction mechanism but proceeds without the formation of radicals and the reaction terminates with formation of an alcohol.

(b) Methane Monoxygenases

The enzymes isolated from methane oxidising bacteria are known under the general name of methane monoxygenases.[1,135–137] The oxidation takes place in accordance with the scheme

$$CH_4 + O_2 + AH_2 \rightarrow CH_3OH + H_2O + A\ , \qquad (32)$$

where AH_2 = NADH or NADPH. The methane monoxygenases isolated from *Methylococcus capsulatus* and *Methylosinus trichosporium* contains proteins incorporating non-haem iron and possibly copper.[1] The enzymes also include cytochrome c, but its presence does not influence the activity of methane monoxygenases. The enzyme from *M. capsulatus* oxidises alkanes ranging from methane to butane and, as the chain length increases, the rate of oxidation falls. Pentane, cyclohexane, and aromatic hydrocarbons are not oxidised.[137] We may note that the activity maximum for cytochrome P-450 corresponds to alkanes containing 8 and 12 carbon atoms. The difference in the activity is apparently associated with the size of the hydrophobic pocket in the enzyme where oxidation takes place and not with a change in the reaction mechanism.

2. Chemical Models

(a) "Direct" Oxidation by High-Valence Metal Compounds

Aromatic, aromatic alkyl-substituted, and saturated hydrocarbons are oxidised by cobalt(III) compounds.[1,11,14,15,138,139] For example, cobalt(III) trifluoroacetate oxidises cyclohexane in solution in CF_3COOH at 30 °C in the course of 23 h to cyclohexyl trifluoroacetate in 35% yield. The proposed mechanism includes the formation of the $R^{\cdot}$ radical from the hydrocarbon RH under the conditions of the elimination of a proton synchronous with the reduction of cobalt(III):

$$RH + Co(III) \rightarrow R^{\cdot} + H^+ + Co(II)\ , \qquad (33)$$

or in the decomposition of the alkyl σ-complex of cobalt(III):

$$RH + CoX_3^+ \xrightarrow{-H^+} RCoX_3 \rightarrow R^{\cdot} + CoX_3\ . \qquad (34)$$

The radicals enter into further reactions leading to the formation of the final products. Numerous studies of the direct oxidation of alkanes and aromatic alkyl-substituted hydrocarbons by compounds of other high-valence metals are known. Thus, on interaction with manganese(III) or lead(IV) acetates in CF_3COOH, adamantane produces 1-adamantyl trifluoroacetate.[140] Lead(IV) acetate oxidises n-heptane and other alkanes at room temperature[12,141] and copper(III) complexes convert cyclohexane into cyclohexanol, cyclohexanone, and benzene in aqueous solution at room temperature.[142]

In highly acid media, in particular in concentrated H_2SO_4, certain complexes, for example those of palladium(II), platinum(III), and mercury(II), oxidise alkanes with formation of olefins, aromatic compounds, and carbonium ions.[143,144] The reactions with all oxidants in acid media apparently have a similar mechanism in the rate-limiting stage—homolytic cleavage of the C–H bond with participation of the ligand L:[143]

$$RH + L^-M^n \rightarrow R^{\cdot} + HL + M^{n-1}\ . \qquad (35)$$

(b) Oxidation by the Oxo-Compounds of High-Valence Metals

There is some similarity between the oxidation of alkanes and other compounds by monoxygenases, on the one hand, and the oxygen derivatives of high-valence metals, on the other. For example, the migration of the substituent, analogous to the NIH shift,[124] has been observed in the hydroxylation of arenes by the chromium(VI) derivatives $CrO_2(OAc)_2$.[124] The reactions of alkanes with chromium(VI) oxo-compounds apparently take place with the intermediate formation of radicals:

$$RH + O{=}Cr^{VI} \rightarrow R^{\cdot} + HO{-}Cr^{V}\ . \qquad (36)$$

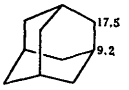
However, not all the radicals formed are liberated in the solution, since the oxidation of (+)-3-methylheptane by chromic acid involves the formation of (+)-3-methyl-3-heptanol with retention of configuration to the extent of 70–85%. The normal selectivity has been observed in the hydroxylation of branched alkanes. The addition of ruthenium(IV) or iridium(IV) chloride complexes increases the rate of the reaction leading to the formation of the chloroalkanes.[145–147] The selectivity of the oxidation in the presence of ruthenium(IV) (1° : 2° : 3° = 1 : 100 : 1000) is different from that in the oxidation catalysed by iridium(IV) (1 : 30 : 250); in the latter case, the primary C–H bond is relatively more reactive. One of the possible causes of the greater oxidising capacity of chromium(VI) compounds is the formation of the mixed complex $[Cl_4RuOCrO_3]^{3-}$.[147] Strong acids accelerate the reaction similarly (the rate of oxidation is proportional to the acidity of the medium), giving rise to protonated species, for example $O = Cr(OH)_3^+$ and $HCrO_3^+$. In solution in $CF_3.COOH$, permanganate oxidises alkanes at room temperature.[148] The cation MnO_3^+ is apparently the active species. The selectivity of the reaction corresponds to 1° : 2° : 3° = 1 : 60 : 2100. Finally, we may note that the ruthenium(IV) complex $[Ru(terpyridyl)(bipyridyl)(O)]^{2+}$ catalyses the electrochemical oxidation of aromatic alkyl-substituted hydrocarbons to alcohols, ketones, and acids.[149]

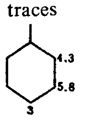
(c) Oxidation of Alkanes Coupled with the Oxidation of Metal Compounds

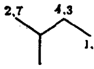
A whole series of systems hydroxylating organic substrates in a process coupled with the oxidation of a low-valence metal derivative by oxygen are regarded as chemical models of monoxygenases. Copper(I), titanium(III), molybdenum(O), molybdenum(III), iron(II), etc. compounds have been used for this purpose.[1] The hydroxylation of alkanes by oxygen in the presence of $SnCl_2$ in acetonitrile at room temperature has been studied in greatest detail.[1,150] The reaction selectivity corresponds to 1° : 2° : 3° = 1 : 5.1 : 12.5. It has been established that the interaction of O_2 with $SnCl_2$ involves a branched chain mechanism with formation of hydroxy-radicals, which react with alkanes.

(d) The GiF System

Molecular oxygen effectively oxidises alkanes in the presence of powdered iron, a carboxylic acid, pyridine, and water (the so called GiF system).[151] It was noted in the first studies that traces of H_2S initiate the reaction.[152,153] Soluble iron complexes are active in the system and zinc dust can be used as the source of electrons.[151,154] Oxidation in the course of 15–20 h at 30 °C leads to the formation of ketones and aldehydes (or an alcohol in the case of a tertiary C–H bond) with the following yields expressed as percentages (indicated by numbers opposite the corresponding positions within the molecule):



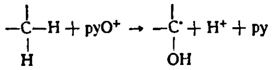




It has been suggested that the unusual selectivity of the oxidation reaction (the low reactivity of a weak tertiary bond compared with the primary and secondary bonds) is associated with the involvement in the process of a carbene complex of iron as an intermediate, but it has been shown[155,156] that the selectivity is independent of the nature of the metal. When copper, tin, and cobalt were used instead of iron, (and in general in the absence of a metal in the initiation of the oxidation) similar results were achieved. The unusual selectivity is apparently determined by the formation of the radicals $HO_2^{\bullet}$ or $RO_2^{\bullet}$ in the presence of pyridine and acid (part of the pyridine should be protonated). It has been suggested[155,156] that the "solvated oxygen cation" pyO^+ (or $pyO^{\ddagger}$), formed from $HO_2^{\bullet}$ or $RO_2^{\bullet}$ in the presence of protonated pyridine, is active in the oxidation of alkanes:

$$HO_2^{\bullet} + pyH^+ \rightleftarrows H_2O + pyO^+ \ . \qquad (37)$$

The pyO^+ species can react with the hydrocarbons as a three-electron oxidant with the elimination of H^+ from the carbon atom undergoing hydroxylation:

 (38)

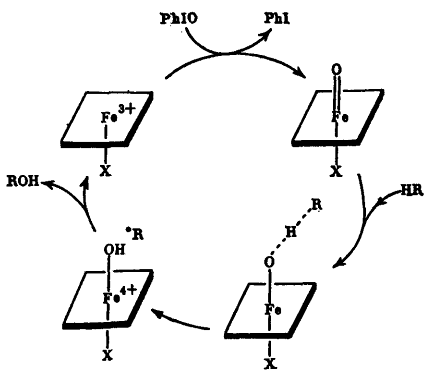
$$-\overset{|}{\underset{\displaystyle\overset{|}{H}}{C}}-H + pyO^+ \rightarrow -\overset{|}{\underset{\displaystyle\overset{|}{OH}}{C^{\bullet}}} + H^+ + py \ . \qquad (38)$$

The radical formed is converted into a ketone or an aldehyde on further oxidation or into an alcohol on reduction. Naturally, this mechanism does not operate in the case of a tertiary C–H bond, which may account for the unusual selectivity of the oxidation process.

(e) Oxidation by Metalloporphyrin Complexes of Oxygen

The closest models of the hydroxylating system based on cytochrome P-450 are oxygen derivatives of metalloporphyrins. Mainly oxidation with participation of iron and manganese complexes, using O_2, iodosobenzene PhIO, and KO_2 as sources of atomic oxygen, has been investigated.[157–170] The mechanism of the oxidation of alkanes catalysed by iron-porphyrins involves the initial oxidation of iron(III) with the simultaneous transfer of an oxygen atom to iron and the formation of the oxoferryl complex $[P{-}Fe^{IV}=O]^+$ (P = porphyrin), which affords an alcohol on reaction with RH (Scheme 4).

Scheme 4



The oxidation of cyclohexane by the PhIO + TPPFeCl system (TPP = tetraphenylporphyrin) leads to the formation of a mixture of cyclohexanol and cyclohexanone in proportions of 15 : 1 in 8% yield. The ratio 3° : 2° = 25–48 : 1. The oxoferryl complex can also be obtained by the interaction of the oxygen complex of iron(III) with the acylating agent AcX (X = OAc, Cl, or OH):[161,165]

$$[P{-}Fe^{III}O_2]^- + AcX \xrightarrow[-X^-]{} P{-}Fe^{III}{-}O{-}O{-}Ac \xrightarrow[-OAc^-]{} [P{-}Fe^{IV}{=}O]^{\ddagger} . \qquad (39)$$

It is of interest that the use of the tetramesitylporphyrin (TMP) complex, in which approach to the iron atom is sterically hindered, makes it possible to alter the selectivity.[165] Thus, whereas 1° : 2° : 3° = 1 : 12 : 40 for the hydroxylation of isopentane in the presence of the TPP-complex while C(1) : C(2) : C(3) = 1 : 10 : 10 for hexane, the corresponding ratios obtained in the presence of the TMP-complex were respectively 1 : 6 : 16 and 1 : 7 : 3. By increasing the steric shielding of the active centre, it is possible to achieve an even greater change in the selectivity. Particles of the tetrakis(p-hexadecyloxyphenyl)-porphyriniron chloride–PhIO–cyclodextrin system, dispersed in aqueous solution, were used as a model of the active centre of cytochrome P-450. Iron-porphyrin is incorporated in the liposomes formed by dimyristoylphosphatidylcholine. In the hydroxylation of hexane, we have the ratios C(3) : C(2) : C(1) = 1 : 1.8 : 0.59 when β-cyclodextrin is used and 1 : 2.1 : 0.77 for permethylated β-cyclodextrin.[166] These results confirm the hypothesis concerning the cause of the unusual selectivity observed in many instances of the biological oxidation of alkanes, according to which the high reactivity of the ω- and (ω – 1)–C–H bond is due to the steric hindrance generated around the active centre of cytochrome P-450.

The system based on the nickel(II) complex with a macrocyclic nitrogen-containing ligand, which hydroxylates arenes, is close to the metalloporphyrin models.[171] The complex forms an adduct with O_2 in aqueous solution, which then oxidises benzene.

V. THE MECHANISMS OF THE CLEAVAGE OF THE C–H BOND

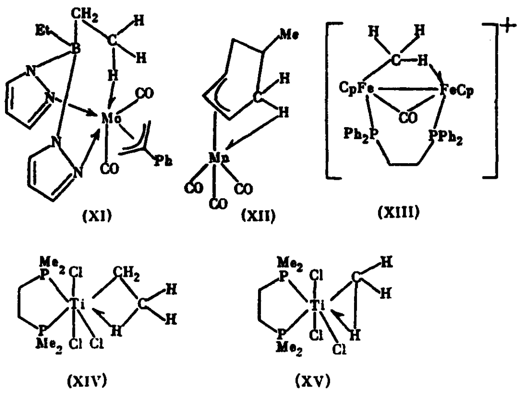
1. Saturated Hydrocarbons and Their Fragments as Ligands in Complexes

From the standpoint of the usual ideas, the formation of any complexes by saturated hydrocarbons is impossible owing to the lack of π or n-electrons in their molecules. However, compounds containing hydrogen and other three-centre bonds,[172] for example B...H...B and Al...CH_3...Al, are well known and fairly stable complexes of molecular hydrogen, namely $(iso\text{-}Pr_3P)_2(CO)_3W(H_2)$ [173] and $Cr(CO)_5(H_2)$,[174,175] have been characterised recently. If these data are taken into account, one can imagine the possibility of the existence of complexes of alkanes. On the other hand, bearing in mind that saturated hydrocarbons are extremely weak electron donors and poor electron acceptors,[176] one can postulate that alkane complexes should be extremely unstable. Thus, when iodine or oxygen is dissolved in saturated hydrocarbons, contact donor–acceptor complexes are formed,[177] the equilibrium formation constant of which is close to zero. The bond energy in these complexes is very low and both components are oriented with respect to one another in an arbitrary fashion. A quantum-chemical calculation for the $CH_4 + O_2$ system showed that,[178] if the C–H σ-bond is located along the axis of the π orbital of oxygen in such a way that the O...H distance is 2.05 Å, a minimum corresponding to a bond energy between the components of ~0.5 kcal mol^{-1} appears on the potential curve. The paramagnetic shifts of the ^{13}C NMR signals, induced by a nitroxy-radical (the di-t-butylnitroxy-radical) dissolved in the saturated hydrocarbon, indicate the formation of a complex between the radical and the alkane.[178,179] The paramagnetic shift $\Delta\delta$ diminishes on passing from the terminal atom of n-pentane to atoms in the 2- and 3-positions. Thus, at a radical concentration of 1 M, $\Delta\delta$ = 3.8, 2.4, and 2.3 p.p.m. respectively. In the case of 2,2-dimethylbutane, the paramagnetic shifts of the signal due to the CH_3 groups in the t-butyl and ethyl fragments are respectively 3.1 and 3.4 p.p.m., the shift for CH_2 amounts to 2.3 p.p.m., while for a quaternary carbon atom it is only 0.13 p.p.m. All the shifts are directed downfield, which indicates a transfer from the radical to the carbon atoms of alkanes having a positive spin density. The data presented led to the conclusion that an alkane forms a complex by interacting via its hydrogen atoms with the π orbital of the radical occupied by the unpaired electron and distributed approximately equally between the N and O atoms. According to the calculation for the model system $CH_3H...ONH_2$ by the INDO method,† the stabilisation energy of the complex for a O...H distance of ~2.0 Å does not exceed 1 kcal mol^{-1}.[181]

(a) Diffraction and Spectroscopic Studies

Fairly numerous complexes in which there is an intermolecular bond between the metal atom and one of the CH groups of the ligand according to X-ray diffraction data, confirmed by infrared and NMR spectra, have been discovered in recent years.[182] The bonds formed by saturated hydrocarbon fragments, especially methyl groups, are of special interest. It has been suggested[182] that such a bond be referred to as "agostic" and to designate it by half an arrow: C–H ⇀ M. Thus the term "agostic" bond refers to the case where the hydrogen atom is simultaneously bound covalently by a three-centre two-electron bond to carbon and transition metal atoms. Scheme 5 presents examples of complexes containing the agostic C–H ⇀ M bond. The presence of an agostic bond in the complexes has been demonstrated by X-ray diffraction (XD) and neutral diffraction (ND) methods.

Scheme 5



Certain distances in the crystal, determined by these methods, are presented in Table 3. When the agostic bond is formed, the C–H bond usually lengthens by 5–10%, but in the case where it is formed by the $C(sp^3)$–H fragment virtually no increase in length is observed. The M–H bond is also somewhat longer (by 15–20%) than in the usual hydride. The M–C bond length is always appreciably smaller than the sum of the van der Waals radii of M and C. The appearance of the agostic bond is reflected in the NMR spectra (upfield shift of the ^1H and ^{13}C signals) and IR spectra (decrease of the stretching vibration frequency of the C–H bond to 2700–2350 cm^{-1}). Thus a system with a C–H ⇀ M agostic bond is, as it were, on the reaction pathway between the C–H + M system and the alkyl hydride derivative C–M–H.

Table 3. Certain interatomic distances in complexes containing the agostic C–H ⇀ M bond.[182,183]

Complex	Method	Distance, A		
		C–H	M–H	M–C
(XI)	XD	0.97(8)	2.27(8)	3.06
(XII)	ND	1.19(1)	1.84(1)	2.34(1)
(XIII)	XD	1.06(4)	1.64(4)	2.101(3)
(XIV)	XD	1.02	2.29	2.516(10)
(XV)	XD	1.00(2)	2.03(4)	2.149(5)
(XV)	ND		2.45	

Dissolution of chromium trisacetylacetonate in 1-chlorobutane entails a paramagnetic shift of the ^{13}C signals of the solvent in the NMR spectra.[184] It is of interest that the shift $\Delta\delta$ along the chain initially diminishes and then again increases for the terminal CH_3 group; the ratios of the $\Delta\delta$ are C(1) : C(2) : C(3) : C(4) = 1.00 : 0.30 : 0.14 : 0.62. These results indicate the transfer of electron spin density from the complex to the methyl group of the chlorobutane coordinated to it and, since the complex is coordination-saturated, the interaction apparently takes place via the acetylacetonate ligand of the complex (outer-sphere coordination). The formation of adducts of cyclohexane with the paramagnetic bis[hydrotris(1-pyrazolyl)borato]cobalt(II) complex has been observed[185] by ^1H NMR.

Finally the formation of methane, hexane, and methylcyclohexane complexes with the $Cr(CO)_5$ species in a matrix has been detected.[186–188]

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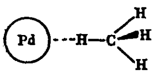
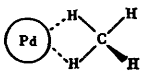
† For the description of different quantum-chemical methods for calculations on molecules, the molecular structure of coordination compounds, the symmetry-based classification of orbitals, etc., see, for example, Minkin et al.[180]

(b) Quantum-Chemical Calculations for Complex Formation

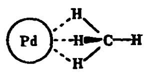
The problem of the coordination of saturated hydrocarbons or molecular fragments to metal complexes has recently attracted the attention of theoretical chemists. It has been suggested that the interaction of saturated C–H bonds with transition metals is due to the overlap of the diffuse outer orbitals of the transition metal with the localised orbitals of the saturated bond.[189,190] The simplest system modelling the interaction of the C–H bond with an unoccupied diffuse orbital of the metal is a CH_4 molecule coordinated to a palladium atom. A calculation has been carried out for this system by the non-empirical SCF MO method.[191] Three possible symmetrical structures, differing in the number of hydrogen atoms coordinated directly to the Pd atom, were examined: two structures with the C_{3v} symmetry [(XVI) and (XVIII)] and one with the C_{2v} symmetry [structure (XVII)]:



(XVI)



(XVII)



(XVIII)

The calculated $CH_4...Pd$ bond energies decrease in the sequence (XVI) > (XVII) > (XVIII), although they are similar for all three structures [8.4 and 7.3 kcal mol^{-1} for (XVI) and (XVIII) respectively]. Coordination leads to a slight transfer of electron density from methane (mainly from H atoms) to the 5*s* and 5*p* orbitals of palladium via a donor–acceptor mechanism; this entails some redistribution of electron density in the individual AO of both components. Thus the electron density in the $4d_{z^2}$ AO of the palladium atom decreases in all three structures. There is a simultaneous increase of electron density in the 5*s*, $5p_\pi$, and $5p_\sigma$ AO but the overall negative effective charge on palladium increases. The changes in the populations of the AO of methane (much smaller) show that the electron density is to some extent transferred also via a dative mechanism. Since a carbon and not a hydrogen atom plays the main role in structure (XVIII), where the methane molecule is oriented towards the palladium atom via three hydrogen atoms [the equilibrium Pd...H distance in (XVIII) is 2.2 Å against 1.7 Å in (XVI)], the dative transfer of electron density from palladium mainly to a carbon atom is most clearly expressed precisely in this structure.

It is of interest that the bond energy in the $Pd...H_2$ system, calculated by the same method, is almost twice as high as the bond energy in the methane complex. The donor–acceptor transfer in the alkane complex is much smaller than in the complex with H_2. On the other hand, in general, since the HOMO energy in CH_4 is higher than in H_2 (the ionisation potentials are 12.7 and 15.4 eV respectively), methane should be a better electron donor. However, according to the calculation, the opposite behaviour obtains. One can therefore conclude that the interaction is in this instance determined by the overlap of the corresponding orbitals and not by the difference between the energy levels.[189,191]

The electronic structure of complexes activating alkanes—square planar and pseudo-square chloride and aquochloride derivatives of platinum(II), as well as the interaction of these complexes with CH_4 have been investigated by the semiempirical MO-LCAO SCF method in the CNDO approximation.[192] Calculation for the complexes $[PtCl_{4-n}(H_2O)_n]^{n-2}$ with $n = 0, 1, 2, 3, 4$ and *trans*-$[PtCl_2(H_2O)(OH)]^-$ showed that the changes in their quantum-chemical characteristics are monotonic and are independent of the symmetry (thus the positive charge on platinum increases monotonically with the increase of *n*). It was concluded that, when the interaction of such complexes with an axial ligand is controlled by the LUMO, then this is an interaction with an *s* AO and to a lesser extent a d_{z^2} AO of platinum. The methane molecule was considered as the ligand and the calculation was performed for the $CH_4...PtCl_4^{2-}$, $CH_4...$*trans*-$PtCl_2(H_2O)(OH^-)$, $CH_4...$*trans*-$PtCl_2(H_2O)_2$, and $CH_4...Pt(H_2O)_4^{2+}$ systems. It was found that coordination involves a redistribution of electron density in CH_4, as a result of which the polarity of the CH bonds increases and the bonds (particularly those coordinated to Pt or an equatorial *acido*-ligand) are weakened. Furthermore, an increase in the free valence of the carbon atom of methane was noted. This actually results in the activation of the CH_4 molecule, facilitating the attack on the latter by polar species. Analysis of the distribution of electron density in methane complexes showed that the alkane is bound as a result of the interaction of the 1*s* AO of the hydrogen atoms and the 2*s* and $2p_z$ AO of the carbon atom with the 6*s* and $6p_z$ AO of platinum. Thus the involvement of the *d* AO of the metal in such complex formation is smaller than the involvement of the outer *s* and *p* AO. For virtually any mode of coordination of CH_4 to the platinum(II) complex (coordination via the vertex, edge, and face of the methane tetrahedron to platinum and also simultaneously to platinum and the acido-ligand was considered), the resulting transfer of electron density from methane entails its decrease at the H atoms. However, owing to the contribution by the dative interaction, the electron density on the carbon atom increases. It is essential to note that the acceleration of the H–D exchange reaction, observed experimentally after the replacement of the $PtCl_4^{2-}$ or $Pt(H_2O)_4^{2+}$ catalysts by $PtCl_2(H_2O)_2$, could not be related to any calculated quantum-chemical parameters. It was therefore postulated[192] that an optimum combination of the donor–acceptor and dative mechanisms of the transfer of electron density is essential for the effective alkane–platinum(II) complex interaction. Since the contribution of the former increases and that of the latter diminishes with increase of the positive charge on the complex, the optimum combination can be achieved for the complex with zero charge. Somewhat earlier the presence of a catalytic activity maximum for the complex $PtCl_2(H_2O)_2$ was attributed to the influence of the symmetry of the ligand environment.[193] On the basis of the hypothesis that the formation of a bond with the activated alkane takes place mainly on interaction with the d_{z^2} AO of the complex, the rates of reaction were correlated with the contribution by this orbital to the LUMO of the platinum(II) complex. Symmetry considerations led to the conclusion that, for $n = 0$ and $n = 4$, the LUMO of the complex is formed solely by the $d_{x^2-y^2}$ AO and cannot contain an admixture of the d_{z^2} state. As a consequence of the decrease of symmetry for $n = 1, 2, 3$, such admixture exists but the $n = 2$ complex occupies a special place (thus the contribution of the d_{z^2} AO orbital for the *trans*-isomer with $n = 2$ should be greatest). It is believed[192] that this approach, based on the crystal field theory, is insufficiently complete, since, according to the MO theory, the d_{z^2} AO of platinum participates in the binding of equatorial ligands even in highly symmetrical complexes, i.e. in these complexes too this orbital, being partly unoccupied, can be involved in the donor–acceptor interaction with the alkane.

The total energies have been calculated by the extended Hückel method[194] for alkanes coordinated to the $PtCl_3(H_2O)^-$ species and it has been shown that the coordination of the terminal atom, for example, in pentane, is most preferred. The MO analysis of the agostic interaction in the methyl complexes of metals has been carried out.[195]

2. Types of Reactions

(a) Electrophilic Substitution

Reactions involving the electrophilic substitution of hydrogen in arenes by metal complexes are known for transition metal complexes: Pd(II),[54] Au,[55,195–197] Pt(II),[56] Pt(IV),[38–49] and Rh(III).[198] This series can be extended if account is taken of the cyclometallation reactions.[31,32,199] Arenes are also readily metallated by compounds of the non-transition elements Hg(II), Tl(III), and Pb(IV). All these reactions apparently proceed with the intermediate formation of Wheland complexes. Less information is available about the electrophilic substitution of hydrogen involved in the formation of the C(sp^3)—H bond. For example, reaction (21) between methane and a lutetium(III) complex proceeds in this way. The oxidation of alkanes by palladium(II) complexes in acid media can proceed via the cyclic transition state in which palladium(II) behaves as the electrophile.[200,201] The saturated H_2 molecule can also be split by a transition metal ion via an electrophilic mechanism:[202]

$$H_2 + Cu^{2+} \rightarrow CuH^+ + H^+ \,. \qquad (39a)$$

Analysis of the thermodynamics of electrophilic substitution reactions

$$L_nM + RH \rightarrow L + L_{n-1}M^-—R + H^+ \qquad (40)$$

yielded[176] the expression

$$\Delta E = E_{M-L} - Q^c_L - Q^c_{L_{n-1}M} + Q^c_{L_nM} \qquad (41)$$

(where ΔE is the energy expenditure on the formation of the coordination vacancy and Q^C are the heats of solvation), from which it follows that substitution is favoured by a low bond energy E_{M-L} and a high heat of solvation $Q^C{}_L$.

(b) Oxidative Addition

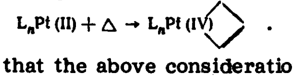
The interaction of arenes with low-valence transition metal complexes, leading to the formation of aryl σ-complexes, is a reaction involving the oxidative addition of the components involved in the Ar—H bond to the metal. The cleavage of the Ar—H bond is usually preceded by the formation of a coordination-unsaturated species via the elimination of hydride, alkyl, and halide ligands. An example of such a process is the insertion of Cp_2W in an aromatic C—H bond[88] (see Section III). The metal complex, to which arenes add via an oxidative mechanism, functions as a nucleophilic species. Thus in the reaction of the complex $HMNp(Me_2.PCH_2CH_2PMe_2)_2$ (Np = 2-naphthyl, M = Fe or Ru) with various arenes, the retarding effect of electron-donating substituents and the accelerating effect of electron-accepting substituents in the aromatic ring was noted. For example, the hydrogen atom in the *para*-position in toluene is 2.5 times more reactive than the D atom in C_6D_6 (where M = Fe).[203] Reactions involving the substitution of hydrogen in aromatic compounds by rhodium(I), iridium(I),[204] manganese(I),[205] rhodium(III), and iridium(III) [206] complexes, which exhibit nucleophilic properties, are known. Examples of the reactions of alkanes, which undoubtedly proceed as oxidative addition, were presented in Section III. The complexes inserted into the aromatic C—H bond are frequently capable of activating also the saturated hydrocarbons or the corresponding fragments via the same mechanism. For example, $HMN_p(Me_2PCH_2CH_2PMe_2)_2$ (M = Fe, Ru, or Os) is inserted oxidatively in the C—H bond of the methyl group of acetonitrile.[207] Estimation of the heat of oxidative addition via the mechanism[202]

$$L_nM + RH \rightarrow R—L_nM—H$$

demonstrated that this reaction is usually endothermic with $\Delta H \cong +10$ kcal mol^{-1} (the following typical dissociation energies were used for the calculation: $D_{M-H} = 60$, $D_{M-R} = 30$, and $D_{R-H} = 100$ kcal mol^{-1} [208]). Oxidative addition with cleavage of the C—C bond via the mechanism

$$L_nM + R—R \rightarrow R—L_nM—R$$

should be thermodynamically even less favourable. This does not apply to the cleavage of C—C bonds in strained hydrocarbons, for example, in the reaction[202]



(42)

It is noteworthy that the above considerations refer to complexes of the first transition series of metals, because there are no data on the bond energies in the complexes of heavier metals. The alkyl—metal bonds can be stronger in the case of heavy metals, although, for example, the D_{M-CH_3} for the M^+—CH_3 ions in the gas phase indicate the absence of a distinct tendency towards an increase of this parameter on passing from light to heavy metals within a given Group.[209] The calculated[210] $\bar{D}_{Pt-C} = 36$ kcal mol^{-1} [for *cis*-$Me_2Pt(PH_3)_2$] and $\bar{D}_{Pt-H} = 60$ kcal mol^{-1} [for *cis*-$(H)_2Pt(PH_3)_2$] made it possible to estimate the enthalpies of the oxidative addition to $Pt(PH_3)_2$ of hydrogen (−16 kcal mol^{-1}, exothermic reaction), methane via the CH_3—H bond (+9 kcal mol^{-1}, which agrees with Halpern's estimate[202]), and ethane via the CH_3—CH_3 bond (+19 kcal mol^{-1}, highly endothermic reaction). On the other hand, the complex *cis*-$OsHMe(CO)_4$ is apparently thermodynamically stable and does not exhibit a tendency towards intermolecular reductive elimination of CH_4 (see below). It has been suggested[202] that the $Os(CO)_4$ species, generated photochemically, is capable of combining oxidatively with the alkanes, this addition process being thermodynamically favourable. Thus the kinetic barrier to the oxidative addition of RH to low-valence metal complexes is fairly low and the inability of many 16-electron complexes to activate alkanes can be associated with the thermodynamic causes.[202] Indeed, the rate of addition of CH_4 to Cp′IrCO depends only very slightly on temperature.[211] The nature of L (CO + PMe_3) has little influence on the reactivity of the complexes Cp′IrL in relation to alkanes, which can also indicate that the activation barrier is low.[202] The energy of the oxidative addition of RH to L_nM is determined by the equation[176]

$$E_{M-R} + E_{M-H} - E_{R-H} \simeq E_{M-M} \qquad (43)$$

and hence can be estimated from E_{M-M}. The highest value of E_{M-M} has been obtained for platinum and in addition it has been shown that the reaction involving Group VIII and I transition metals is energetically favourable.

The components involved in saturated bonds can add oxidatively simultaneously to two metal complex molecules:

$$M + R—R + M \rightarrow 2M—R \,.$$

It may be that reaction (15) proceeds as two-centre oxidative addition of the components of the $(CH_3)_4Sn$ molecule, namely CH_3 and $Sn(CH_3)_3$, to two platinum(II) species. Finally, one cannot rule out the possibility that, in the interaction of the Pt(II) + Pt(IV) system with methane, the methyl group adds oxidatively to the platinum(II) in the molecule, forming $CH_3Pt(IV)$, while the second component, the hydride, reduces platinum(IV) to platinum(II). Information about the oxidative addition mechanism can be obtained from the study of the reverse process—reductive elimination.[212,213] For example, since the interaction of $OsH(CD_3)(CO)_4$ and $OsD.(CH_3)(CO)_4$ results in the formation of a mixture of CH_4, CH_3D, CD_3H, and CD_4, one may conclude that the reductive elimination proceeds as a bimolecular process:

$$2OsH(CH_3)(CO)_4 \rightarrow CH_4 + (OC)_4HOsOs(CH_3)(CO)_4 \,. \qquad (44)$$

However, the reaction is kinetically of first order, i.e. its rate-determining stage is unimolecular. In the presence of amines or phosphines (L = py, PPh_3, or PEt_3) a first order is also observed but the reaction proceeds as intramolecular elimination.[214] At the rate-determining stage, an intramolecular rearrangement takes place with insertion of CO in the $Os-CH_3$ bond. The acyl complex formed reacts in a rapid stage with a second molecule of the initial compound.

Processes involving the oxidative addition of the components involved in the saturated H–H or R–H bonds to metal complexes or metal atoms as well as the reductive elimination of RH have been investigated by quantum-chemical methods.[215–223] We shall consider the general case of the interaction of a metal complex with the simplest saturated molecule, namely H_2.[218] In the interaction of the bonding σ orbital of hydrogen with the unoccupied acceptor orbital of the complex and of the antibonding σ^* orbital with the occupied donor orbital, four orbitals of a new hydride derivative are generated. The two low-lying orbitals are filled with electrons, one being symmetrical and the other antisymmetrical relative to the twofold axis or the mirror symmetry plane. A symmetrical combination is formed, for the MH bond generated, from the occupied orbital of the hydrogen molecule and such electron transfer from $\sigma_g(H_2)$ to ML_n weakens the H–H bond and strengthens the M–H bond. The electron transfer in the opposite direction, namely donor orbital $\rightarrow \sigma_u^*$, also weakens H–H and strengthens M–H. One can assume that the occupied a_1 orbitals and the three degenerate t_2 orbitals in CH_4 correspond to the σ_g orbital of the hydrogen molecule. Since the energy of the t_2 orbital is greater by 2 eV than the energy of the $\sigma_g(H_2)$ orbitals, the CH_4 molecule is a somewhat stronger donor.

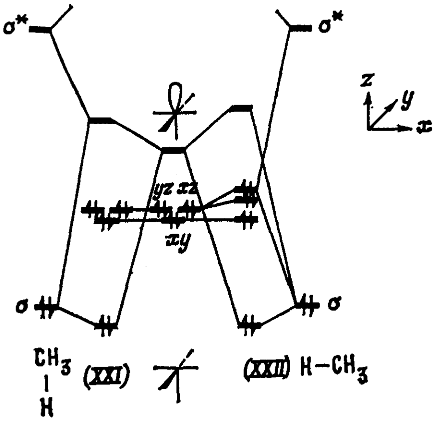
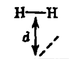


Figure 1. The interaction of orbitals in the formation of the structures (XXI) and (XXII).[218]

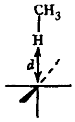
The total energy of the $H_2...Cr(CO)_5$ system has been calculated by the extended Hückel method.[218] The interaction energy is negative for both the perpendicular orientation (XIX) and the parallel orientation (XX) of the H_2 molecule approaching the $Cr(CO)_5$ fragment, which has the C_{4v} symmetry. However, in the case of the parallel approach of H_2 the energy of the system has a much more distinct minimum. When H_2 is replaced by CH_4, the curve for the perpendicular approach has approximately the same form but the parallel approach becomes extremely unfavourable.

Whereas the d_{xz} orbital (which functions as the donor orbital in the complex) is lowered for (XX), in the case of CH_4 [structure (XXII)] the energies of both d_{xz} and d_{yz} orbitals increase (Fig.1).

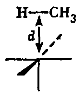
(XIX)



(XX)



(XXI)



(XXII)

If the CH_4 approaches $Cr(CO)_5$ in such a way that the $H-CH_3$ axis forms an angle θ with the height of the pyramid, the structure is stable for $d(M-H) = 2.0$ Å and $\theta \leq 130°$. However, the perpendicular orientation ($\theta = 180°$) remains the most favourable. The reactions involving the oxidative addition of H_2 and CH_4 to $Rh(CO)_4^+$ and the corresponding isolobal complex CpRh(CO) and to the metallic surfaces of nickel and titanium have also been analysed.[218]

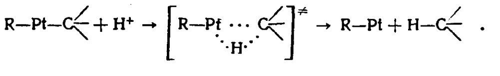
(c) The Mechanism with a Three-Centre Transition State

The first stage in the reaction of alkanes with the platinum(II) complex proceeds via a mechanism which cannot apparently be identified with either typical oxidative addition or the usual electrophilic substitution. Indeed the correlation (2) yields $\rho^* = -1.4$, indicating weak electrophilic properties of the metal complex. On the other hand, the series characterising the influence of ligands on the rate of the H–D exchange [reaction (1)] is the opposite to the *trans*-effect ligand series for the substitution reaction, which takes place with square platinum(II) complexes, but this does not agree with the mechanism involving the direct substitution of the ligand at platinum(II) by the alkane:

$$RH + Pt(II){-}Cl \rightarrow [H \cdots R \cdots Pt \cdots Cl]^{\neq} \rightarrow H^+ + RPt + Cl^- .$$

We may note that, in the cyclometallation of arenes, the rhodium(I) and iridium(I) complexes behave as nucleophiles, the palladium(II) complex exhibits electrophilic properties, and the platinum(II) complex occupies an intermediate position.[204]

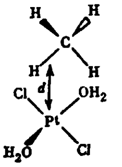
Presumably the reaction of the chloroaquoplatinum(II) complex with alkanes begins as oxidative addition, proceeds through a three-centre transition state, and terminates by the synchronous formation of a Pt–C bond with elimination of H^+ (which can be transferred to a H_2O molecule).[18,176,223] A similar mechanism has been proposed for the cyclometallation of 8-alkylquinolines by palladium(II).[224] It has also been suggested that the reverse process—the protolysis of the Pt(II)–C bond in alkyl and aryl complexes—involves a three-centre transition state:[225–227]



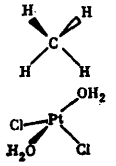
$$R{-}Pt{-}C\!\lessdot + H^+ \rightarrow \left[R{-}Pt \cdots \underset{\cdot\cdot H \cdot\cdot}{C}\!\lessdot\right]^{\neq} \rightarrow R{-}Pt + H{-}C\!\lessdot \quad (45)$$

At the same time the photolysis of the Pt–C bond in *trans*-$[PtH(CH_2CN)(PPh_3)_2]$ takes place in two stages: the oxidative addition of H^+ to the metal and the subsequent elimination of CH_3CN with formation of *trans*-$[PtHCl(PPh_3)_2]$.[228]

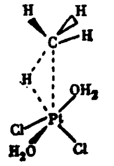
The cleavage of the C–H bond in methane by the *trans*-$PtCl_2(H_2O)_2$ complex has been subjected to quantum-chemical analysis by the extended Hückel method,[176,223] It was shown that the approach of CH_4 to the square planar platinum(II) complex [structure (XXIII)] leads to strong four-electron repulsion, the main cause of which is the interaction between the t_2 orbitals of methane and the occupied orbitals of the metal complex localised in the region of the free coordination site (HOMO consisting mainly of the d_{z^2} orbital and also the low-lying d_{yz} orbital). When the distance between the Pt atom and the centre of the C–H bond reaches $d = 2.8$ Å, the distortion of the metal complex [structure (XXIV)] lowers the repulsion energy. The composition of the HOMO then changes, namely the contribution of the d_{z^2} orbital diminishes and that of the $d_{x^2y^2}$ orbital increases, which entails a decrease of the electron density in the region of the free coordination site. The $d_{x^2-y^2}$ orbital is hybridised with the s, p_z, and d_{z^2} orbitals of the metal, as a result of which the low acceptor MO of the complex becomes extended in the axial direction.



(XXIII)



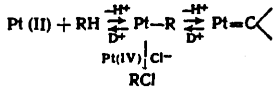
(XXIV)



(XXV)

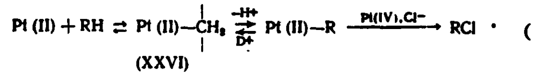
The overlap of the acceptor orbital with the σ orbital of the C–H bond increases and hence the contribution of the transfer of electron density via the donor–acceptor mechanism also increases. This is accompanied by the simultaneous increase of the dative interaction, the main contribution to which is made by the charge transfer from the d_{z^2} and d_{yz} orbitals to the σ* orbitals of methane. In the second stage, the deformation distortion of the methane molecule occurs starting with $d = 2.4$ Å and the repulsion energy diminishes still further. At the same time the angle of the displacement of the ligands from the plane of the complex increases from 10° to 36°. The populations of the Pt–C and Pt–H bonds reach 30–40% and the C–H bond is loosened to the extent of 20–30%. Under these conditions, the overlap of the d_{yz} and t_2 orbitals diminishes. Since an analogue of an unshared pair oriented towards the complex appears at the carbon atom, namely the $3a'$ component at the t_2 level (Fig. 2), the donor–acceptor interaction is enhanced. The transition state (XXV) arises for $d = 1.8$ Å, whereupon the Pt–C and Pt–H bond lengths reach the usual values and the angle of deviation of the ligand in the complex is 36°. When the C–H bond is extended by 0.28 Å, a maximum appears on the curve describing the energy of the system and the C–H, Pt–C, and Pt–H bonds become approximately equivalent. The extension of the C–H bond enhances both the donor–acceptor and dative interactions; the main contribution to the latter comes in this case from the transfer of electron density to the $3a_1$ component of the t_2^* level. This transfer plays a decisive role in the rupture of the C–H bond. It is noteworthy that, when the C–H bond is extended, the four-electron repulsion increases faster than the interactions of both types and only when CH_4 and the complex are close together do the repulsion and dative interaction energies become equalised. Calculation[223] has shown that, on passing from *trans*--$PtCl_2(H_2O)_2$ to $PtCl_4^{2-}$, the activation energy for the reaction with the alkane should increase by 0.24 eV, which agrees with the experimental data (these yield a difference ⩾0.17 eV). In the first stages of the process, up to the appearance of the transition state, the C–H bond is polarised, which increases the acidity of the hydrogen atom. This is apparently why in the presence of bases stronger than the platinum(II) complex, it is easier for the system to transfer hydrogen in the form of H^+ to the molecule of the base, which may be H_2O. Thus the reaction may be completed by the synchronous formation of the Pt–C bond and the elimination of H^+, i.e. can proceed as "soft" electrophilic substitution.

The study of the kinetics of the H–D exchange and of the oxidation of alkanes as well as the analysis of the multiple exchange parameter led to the hypothesis[229] that the reaction does not proceed via the alkyl–carbene mechanism



$$\mathrm{Pt(II)} + \mathrm{RH} \underset{D^+}{\overset{-H^+}{\rightleftarrows}} \underset{\mathrm{RCl}}{\underset{\downarrow\,\mathrm{Pt(IV)},\,\mathrm{Cl^-}}{\mathrm{Pt{-}R}}} \underset{D^+}{\overset{-H^+}{\rightleftarrows}} \mathrm{Pt{=}C}\!< \qquad (46)$$

but via the alkane–alkyl mechanism



$$\mathrm{Pt(II)} + \mathrm{RH} \rightleftarrows \underset{\mathrm{(XXVI)}}{\mathrm{Pt(II){-}CH_3}} \underset{D^+}{\overset{-H^+}{\rightleftarrows}} \mathrm{Pt(II){-}R} \xrightarrow{\mathrm{Pt(IV),Cl^-}} \mathrm{RCl}\ . \qquad (47)$$

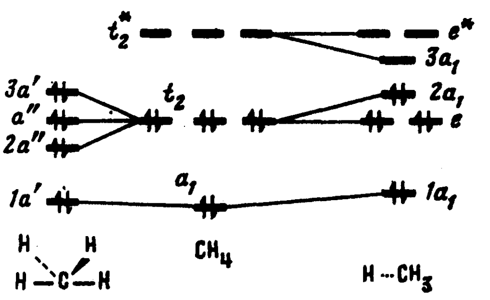
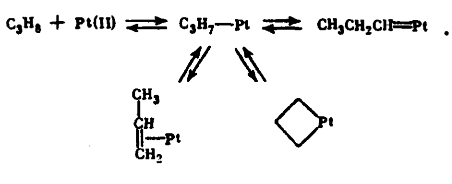


Figure 2. The change in the orbitals of the methane molecule on deformation of the angles and following an increase in the C–H bond length.[223]

It has been suggested that the first kinetically significant intermediate in this reaction is the Pt(II)–alkane complex (XXVI), which is an analogue of alkonium ions of the type CH_5^+, whose formation is associated with the deformation of both the planar complex and of the tetrahedral hydrocarbon molecule. The multiple H–D exchange in alkanes under the influence of platinum(II) can also be due to the formation of olefinic π-complexes and metallocycles[1] (Scheme 6).

Scheme 6



(d) Cleavage with Formation of Radicals

In contrast to the activation of an alkane by a platinum(II) complex, the reaction of RH with Pd^{2+} may begin as electron transfer.[230] The hydroxylation of alkanes by oxygen complexes also proceeds with formation of radicals (see Section IV). In the latter case the interaction of the metal with the C–H bond takes place via a bridging ligand.[143,144,231,232] The formation of a benzylrhodium(III) σ-complex on interaction of the porphyrinrhodium dimer with toluene apparently begins with attack by the P–Rh(II)• radical species on the C–H bond.[233] The reaction of $PtCl_6^{2-}$ with hexane induced by light or γ-radiation[26–29] begins with the homolysis of the Pt–Cl bond in the excited species $[PtCl_6^{2-}]^*$,[234–236] which results in the formation of a platinum(III) complex and the $Cl^{\bullet}$ radical species. The latter can apparently attack the hexane molecule in the solvent (CH_3COOH) cage. The hexyl radical formed recombines with $Pt^{III}Cl_5^{2-}$ to produce a hexylplatinum(IV) σ-complex, which eliminates HCl reductively and is converted into the hexeneplatinum(II) π-complex. The hexyl radical can also be oxidised or can disproportionate with formation of hexene. The olefin readily reacts with[237] the platinum(II) or platinum(IV) chloride complex, affording the hexene π-derivative.

3. Polar, Orbital, and Steric Control

The reactions of metal complexes and other reagents with saturated compounds containing a C–H bond can be subdivided into three types depending on the factors which have a decisive effect on the course of the process. According to perturbation theory,[238] the total energy change ΔE on partial formation of a bond between the atom s of an electron-donating molecule S and the atom t of an electron-accepting molecule T in a solvent with an effective dielectric constant ε is expressed by an equation incorporating the electrostatic and covalent terms:

$$\Delta E = -\frac{q_s q_t}{R_{st}\varepsilon} + \frac{2(c_s^m c_t^n \Delta\beta_{st})^2}{E_m^* - E_n^*}, \qquad (48)$$

where q_s and q_t are the total charges on the atoms s and t in the isolated molecules, R_{st} is the distance between the atoms s and t, c_s^m and c_t^n are the coefficients of the corresponding AO, $\Delta\beta_{st}$ is the change in the resonance integral on interaction of the orbitals of the atoms s and t, and E^* are quantities characterising the energies of different MO in the isolated molecules.

When atoms carrying large opposite charges interact, an increase in the contribution of the first, electrostatic term in Eqn.(48) favours the reaction. If the difference between the energy levels of the occupied MO of the donor and the unoccupied MO of the acceptor is large, the contribution of the covalent term is insignificant. Interactions of this type refer to reactions controlled by the charge (polar control).[238] In order that alkanes, which are weak donors, should enter into reactions of this type, very strong acceptors are required. Here one can apparently include the reactions of alkanes with complexes of metals in a high oxidation state. The variation of the selectivity in the sequence 3° ≫ 2° ≫ 1° is characteristic of such processes involving alkanes. In this case the role of the medium (especially the acidity) is large. The C–H bond in arenes is cleaved much more readily than in alkanes. Clearly this class includes typical electrophilic substitution reactions. On the other hand, if the HOMO of the donor and the LUMO of the acceptor have very similar energies, the denominator $E_m^* - E_n^*$ becomes extremely small and the second term in Eqn.(48) is very large. Such processes are classified as orbital-controlled. The reactions of alkanes with complexes of metals in low and moderate oxidation states [for example platinum(II), iridium(I), and rhodium(I)] are close to this type. The energy of the metal–carbon bond formed and of the C–H bond ruptured should be particularly important in this connection. Polar factors are not then significant and the influence of the medium is usually small. Bearing in mind that the changes in the M–C and C–H bonds cancel out, the selectivity as regards the point of attack on the molecule is low and different molecules with the C–H bond have similar reactivities. Finally, steric factors can play a decisive role in the process. In this case the selectivity series are of the type 1° > 2° ≫ 3° and $\omega > (\omega - 1) \gg (\omega - 2)$; methane may prove to be the most reactive molecule. Biological oxidation is apparently closest to processes of this type, although steric factors are also clearly important in reactions involving metal complexes.

In the real processes involving alkanes account must be taken of all three factors. Their quantitative assessment for different reactions still needs to be carried out.

VI. CONCLUSION

During the 18 years which have elapsed since the discovery of the first reactions of alkanes in solutions of metal complexes, this field of chemistry has developed vigorously, particularly in recent times. There is no doubt that one may expect the discovery of new, especially catalytic, processes with participation of methane and its homologues, which will find practical applications. In its turn, this will intensify the interest in alkanes from the standpoint of their involvement in selective chemical processes and the new chemistry of alkanes thus established will be in line with the ever more urgent need for economy in the consumption of the existing resources of this chemical raw material on our planet, which have accumulated during the billions of years of its existence.

The rapid development of this field of chemistry is also reflected in the fact that, during the period required to prepare the manuscript of this review for the press, several tens of articles solely or partly devoted to the activation of the C–H bond in hydrocarbons and dealing with related problems have appeared in the literature. Reviews have been published on individual problems of the activation of alkanes by metal complexes.[239–244]

The reactions of the hydride, cyclopentadienyl, and other complexes of transition metals in a low oxidation state with alkanes,[245–252] olefins,[253–256] and arenes,[257–260] which proceed as a rule via the oxidative addition mechanism, have been investigated vigorously. The complexes catalyse the H–D exchange in methane[245,246] and benzene.[246,257] Organyl σ-derivatives can be isolated in the case of rhenium,[247,251] thorium,[248] iridium,[249,254–256,258] rhodium,[250] platinum,[252] iron,[253] and osmium[260] complexes. Evidence has been obtained that the addition of an alkane to the $C_5Me_5RhPMe_3$ species takes place with the intermediate formation of an alkane η^2-complex (with an agostic bond).[250] Factors promoting the initial activation of the C–H bond have been discussed.[261] The iridium hydride complex catalyses the thermal and photochemical alkane dehydrogenation reaction.[262] The possibility of hydromethylating carbon monoxide (with formation of acetaldehyde from CH_4 and CO or ethyl methyl ketone from CH_4, CO, and C_2H_4) in the presence of the Cp_2TiCl_2–$(CH_3)_2AlCl$ system has been demonstrated.[263] The reaction involving the "metathesis" of the σ-bonds between the pentamethylcyclopentadienylscandium complex Cp_2^*ScR and the hydrocarbons R'H ($^{13}CH_4$, arenes, and styrenes) via the mechanism $Cp_2^*ScR + R'H \rightleftharpoons Cp_2^*ScR' + RH$ has been described.[264] The bipyridyl complexes of platinum(II) catalyse the addition of methane to acetylene with formation of propene.[265] A number of studies[269–276] have been devoted to cyclomethylation (see the relevant reviews[266]) with cleavage of saturated and aromatic C–H bonds. The thermodynamic and kinetic parameters of the reversible cyclomethylation of the C–H alkyl bonds have been determined[273,274] and the intermolecular cleavage of such bonds in a chelate cobalt complex has been described.[275] The dimers of octaethylporphyrin complexes of rhodium[277] or iridium[278] react with aromatic alkyl-substituted compounds via an aliphatic C–H bond with the simultaneous formation of alkyl σ-derivatives and hydride derivatives (see also Wayland and Del Rossi[233]). The activation of

H–H and C–H bonds by ML_n species with the d^0 configuration, for example, Cp_2LuR, has been analysed by the extended Hückel method.[279] The interaction of the d^6 ML_5 fragments with H_2 involving the η^2-H_2 type of coordination of hydrogen to the metal and the formation of the dihydride derivative, has been investigated by the same method.[280] The dihydrogen complexes $M(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$, where M = Mo or W, have been isolated and characterised.[281] The adducts of saturated hydrocarbons with the paramagnetic complexes $Cr(acac)_3$ and $Fe(acac)_3$ have been detected by ^{13}C NMR in solutions in $CHCl_3$ and CCl_4.[282]

Examples of the cleavage of C–C bonds by metal complexes have been described in a number of studies.[283–286] The reaction of pentamethylcyclopentadiene with $Mn_2(CO)_{10}$ proceeds, in particular, with the cleavage of a C–C bond, which results in the formation of tetramethylcyclopentadienyltricarbonylmanganese.[284] A compound containing a π-bond between iridium and monomethylcyclopentadiene is formed from 1,1-dimethylcyclopentane and the complex $[Ir.(H)_2(Me_2CO)_2L_2]^+$, where $L = (p\text{-}FC_6H_4)_3P$.[285] Cycloalkylrhodium hydride complexes rearrange to rhodacycloalkanes.[286] The reactions of alkanes with transition metal atoms, ions, and complexes in the gas phase and in the matrix at low temperature, which proceed with the cleavage of C–H and C–C bonds, have been described.[287–296]

The interaction of aromatic, alkyl-substituted aromatic, and saturated hydrocarbons with compounds of metals in a high oxidation state usually takes place as electrophilic substitution or involves the formation of radicals. Thus, detailed study of the reactions of arenes with the octaethylporphyrin complex of rhodium(III) in the presence of Ag^+ (this ion eliminates chlorine from the metal complex) has shown[297] that the aryl σ-derivative is formed on electrophilic substitution. The logarithms of the relative rates of methylation of substituted benzenes are correlated with the σ parameters ($\rho = -5.43$). It is of interest that photolysis of solutions of aryl σ-complexes in benzene leads to the homolytic cleavage of the Rh–C bond, which results in the formation of 4-substituted biphenyls.[297] A study has been devoted[298] to the mechanism of the methylation of arenes by mercury(II) and thallium(III) compounds. In a study of the products of the decomposition of the *meta*- and *para*-isomers of the tolylplatinum(IV) σ-complex, formed in the reaction between H_2PtCl_6 and toluene in aqueous CF_3COOH, it was observed that, together with the "expected" 3,3'-, 4,4'-, and 3,4'-bitolyl isomers, a large amount of the 2,3'- and 2,4'-bitolyls is formed after a long induction period.[299] Such products of *ortho*-substitution relative to the methyl group are apparently formed on interaction of *meta*- and *para*-platinised toluenes with free toluene present in solution. It has been shown[300,301] that the oxidation of methylbenzenes by palladium(II) complexes in an acid medium can occur via two pathways: electrophilic substitution in the arene ring with formation of an organometallic intermediate and one-electron transfer from the arene to the palladium atom with participation of the arene radical-cation as an intermediate. The oxidation of mesitylene by the $PtCl_6^{2-}$ ion, which leads to the formation of diarylmethane, apparently takes place with electron transfer.[302] Irradiation by light of a solution of anisole and the $OsCl_6^{2-}$, $IrCl_6^{2-}$, or $RhCl_3$ complex in acetic acid affords a mixture of bianisyl isomers.[303] It has been suggested that in the first stage of the reaction an electron is transferred from the arene to the excited metal complex species and the resulting radical-cation attacks a free anisole molecule.[303] When solutions of the $AuCl_4^-$ [304] or $PtCl_6^{2-}$ [305] ions are irradiated in the presence of alkanes, excited metal complex species are generated,[306] after which the Au–Cl or Pt–Cl bonds undergo homolysis with formation of Cl radical species, which chlorinate alkanes. In the case of $PtCl_6^{2-}$, a hexeneplatinum(II) π-complex is formed as a second reaction product[26–29,305] in addition to the chlorohexane isomers.[305] The reactions involving the free-radical halogenation of alkanes by halogeno-derivatives of hydrocarbons (for example, CCl_4) can be initiated by carbonyl complexes such as $Re_2(CO)_{10}$, $Cr(CO)_6$, etc.[307] The homolytic reactions involving the introduction of functional groups into oxygen-containing compounds are initiated by variable-valence metal derivatives.[308] It has been shown that the oxidation of toluene derivatives by oxygen, catalysed by cobalt acetate in the presence of NaBr, takes place in two stages and that in the first rapid stage chain propagation takes place via the reaction between the peroxy-radical and the cobalt bromide complex.[309] It has been suggested that hydrocarbons are oxidised by lead tetraacetate via a free-radical mechanism.[310] On the other hand, the acyloxylation of toluene by oxygen at the methyl group, catalysed by the $Pd(OAc)_2$–$Cu(OAc)_2$ system, is apparently heterolytic.[311] The activation of a C–H bond in allyldialkylruthenium(IV) complexes has been described.[312]

Several studies have been published on the oxygenation of hydrocarbons by oxygen-containing compounds of high-valence metals. Irradiation of polyoxotungstate by light in the presence of zerovalent platinum and an alkane involves the introduction of a functional group into the hydrocarbon.[313] It has been found that irradiation accelerates the oxidation of alkyl-substituted aromatic hydrocarbons, cyclohexane, and adamantane by oxo-complexes of chromium(VI) both in a homogeneous solution in acetic acid and in water in the presence of tetrabutylammonium bromide.[314] Chromyl trifluoroacetate proved to be an exceptionally powerful oxidising agent capable of oxidising alkanes to ketones at room temperature in solution in CCl_4.[315] Anhydrous $FeCl_3$ in dry acetonitrile activates hydrogen peroxide; the reaction of this system with cyclohexane gives rise to cyclohexyl chloride, cyclohexanol, and cyclohexanone.[316] It has been suggested that the process does not proceed via a radical mechanism. The kinetics and selectivity of the oxidation of alkanes to aromatic hydrocarbons by permanganate in aqueous solutions have been described.[317]

A series of further detailed studies of the Gif system have been published recently.[318–325] The system is effective in the oxidation of natural products, for example, steroids;[318,321–323]; the mechanism of the oxidation has been discussed.[320] The metallic zinc in the oxidising system can be replaced by a cathode (the electrochemical version has been called the Gif–Orsay system).[324,325]

Several studies[330–337] have been devoted to cytochrome P-450 and hydrocarbon oxidation reactions with its participation (see the relevant reviews[326–329]). Increasing attention has been paid to hydrocarbon oxidation reactions catalysed by metalloporphyrins, which model the action of cytochrome P-450 (see the relevant reviews[338–341]). It has been suggested that $KHSO_5$ [342] and NaOCl [343] be used as donors of atomic oxygen in such processes. The stage involving the cleavage of the O–O bond in the porphyrin derivative of iron has been observed;[344] the cleavage of this bond in the analogous manganese(III) complex can take place both heterolytically and homolytically.[345] A change in the selectivity of the oxidation of alkanes with increase of the steric shielding of the active centre of the metalloporphyrin catalyst has been demonstrated in a number of studies.[346–349] Hydrocarbons are oxidised by iodosobenzene in catalysis by phthalocyanine complexes of iron on a zeolite[350] or by oxygen in catalysis by haemin immobilised on the surface of silica.[351]

Finally we may mention several studies on the introduction of functional groups into alkanes without the involvement of metal complexes: photohydroxylation with the aid of H_2O_2,[352] oxidation by peracids[353] and ozone,[354] and the formation of carboxylic acids from alkanes and CO in the HF–SbF$_5$ mixture.[355]

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Reactions of Carbonyl Compounds with Organic Derivatives of Alkali Metals and Hydride Reductants: the Effects of the Medium and the Cation

A.A.Solov'yanov and I.P.Beletskaya

The effects of the medium and the cation in the reactions of alkali metal salts of CH acids and hydride reductants with carbonyl compounds are analysed.
The bibliography includes 73 references.

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I. INTRODUCTION

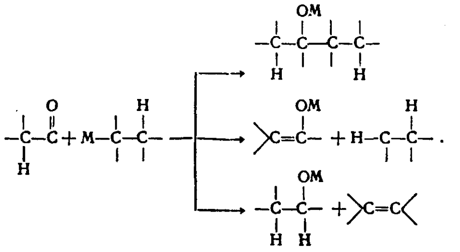
The reactions of carbonyl compounds with organometallic derivatives are widely used in synthetic organic chemistry as one of the main methods for the formation of the carbon–carbon bond. However, despite the enormous number of studies devoted to the practical development of syntheses on the basis of carbonyl compounds, until recently the existing ideas about the mechanisms of these processes were fairly vague. Systematic studies of the influence of the nature of the solvent and the size and charge of the cation on the kinetics and mechanisms of reactions with participation of carbonyl compounds began only in the last decade. Thus, the first model of the mechanism of the reactions of carbonyl compounds with organic derivatives of alkali metals, which is based on the extremely fruitful idea that the carbonyl group can be activated by the coordination of the oxygen atom to a metal cation and that the effective nucleophile (the group R of the organometallic compound) can be deactivated via association with formation of ion pairs, was constructed[1] in 1978. At the same time one must note that this, in essence, kinetic scheme clearly underestimates the thermodynamic factor known from other investigations, in particular, the fact that in the case of a thermodynamically sufficiently stable carbanion the addition to the carbonyl group can be reversible and the thermodynamic stability of the product should also depend on the cation and the solvent. Therefore, precisely at this time, when there has been a growth of interest in problems of the mechanism of the reactions of carbonyl compounds, it is necessary to perform a more detailed analysis of all the factors active in these processes in order to be able to base the formulation of the problems tackled in the later studies on the entire set of theoretical ideas in this field.

This review considers in the first place the reactions of organic derivatives of alkali metals with aldehydes and ketones, which lead to the formation of a C–C bond and for which data are available concerning the influence of the cation and the solvent on the rate and on the yield and composition of the products formed. Precisely for these reactions it is most often possible to relate the thermodynamic and kinetic parameters to the state of the organometallic compounds in solution (the type of ion pairs, the presence of free carbanions, the formation of associated species made up of ion pairs) and the ability of the cations to be coordinated to the carbonyl oxygen, which is of decisive importance for the determination of the process mechanism. An attempt has been made to consider critically the data in the original communications and to interpret them whenever possible from a single standpoint.

It is noteworthy that, from the standpoint of the effects of the medium on the cation, the reactions of organic derivatives of alkali (and alkaline earth) metals with carbonyl compounds and processes involving the reduction of the carbonyl group by alkali metal tetrahydroaluminates and tetrahydroborates have a great deal in common. Frequently the same workers have carried out parallel studies on processes of both types. For this reason, in certain cases, whenever this is necessary for the modelling of individual stages of the reaction or for the establishment of a more general picture, the review presents data on the reactivities of alkali metal enolates and cuprates and organomagnesium compounds and the hydride reduction reactions of the carbonyl group are also considered.

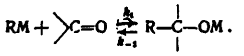
II. REACTIONS OF ORGANIC DERIVATIVES OF ALKALI METALS WITH ALDEHYDES

The reactions of organic derivatives of alkali metals and organomagnesium compounds with carbonyl compounds (aldehydes and ketones) can proceed in principle via three pathways:[2] addition, enolisation (when the carbonyl compound contains a sufficiently mobile proton), and reduction:



The relative contributions of each pathway are determined by the structure of the organometallic and carbonyl compounds, the charge and size of the metal ion M, the nature of the solvent, temperature, and certain other factors. It is simplest to analyse the influence of the reaction conditions on the reaction rate and the final result in the interaction of organic derivatives of alkali metal compounds with aldehydes where only addition products are formed as a rule. However, we shall begin this Section with one of the most important features of the reaction involving addition to the carbonyl group—its reversibility.

The idea of the reversibility of the nucleophilic addition to the carbonyl group probably arose in a study in 1950 of the kinetics of reactions in which organolithium compounds were chosen as nucleophiles.[3] The authors were able to explain the observed features only within the framework of a kinetic scheme including a rapid stage in which the alkoxide formed is cleaved into the initial reactants:

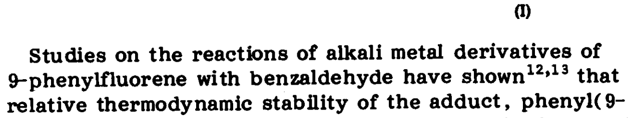


$$RM + {>}C{=}O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R{-}\overset{|}{\underset{|}{C}}{-}OM. \qquad (2)$$

Other investigators observed[4,5] that the ease of the analogous cleavage of alkoxides derived from β-hydroxyesters, namely $PhRC(OM)CH_2COOR'$ (where R = CH_3 and Ph and R′ = C_2H_5, iso-C_3H_7, or t-C_4H_9), obtained by the metallation of the corresponding OH acids by alkali metal amides in toluene, liquid ammonia, and diethyl and dibutyl ethers, depends greatly on the size of the counterion. Thus the yield of benzophenone obtained when $Ph_2C(OM)CH_2COOC_2H_5$ was kept in liquid ammonia for several hours amounted to 89 and 71% for M = Na and K but was 0% when M = Li. The alkoxides $Ph_2CHC(OM)Ph_2$, where M = Na or K, are also cleaved fairly readily in ether and liquid ammonia with formation[6,7] of benzophenone and the alkali metal derivative of diphenylmethane.

According to Cram's data,[8,9] the yield of the acetophenone formed on cleavage of alkoxides having the general formula $(C_2H_5)(CH_3)(Ph)C{-}C(CH_3)(Ph)(OM)$ in dimethyl sulphoxide (DMSO) increases sharply with increase in the radius of the alkali metal cation M: 25% for Li (24 h, 170 °C), 28% for Na (24 h, 75 °C), and 68% for K (12 h, 25 °C). The cleavage of alkali metal derivatives of trialkylcarbinols into the corresponding carbonyl compound and the organic derivative of the alkali metal takes place more effectively the greater the radius of the metal atom: Li < Na < K.[10]

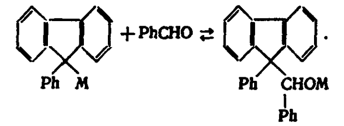
The thermodynamic stability of the alkali metal alkoxide depends not only on the size of the alkali metal cation but also on the solvent. This is indicated by the clear decrease of the yield of the adduct (I) obtained by the addition of 2-lithio-2-phenyl-1,3-dithiane to 4-t-butylcyclohexanone: 90% in cyclohexane, 75% in tetrahydrofuran (THF), and 0% in hexamethylphosphoramide (HMP)† and also by the quantitative decomposition of this compound (obtained beforehand in cyclohexane) into the initial reactants when the solvent is replaced by HMP:



(3)

(I)

Studies on the reactions of alkali metal derivatives of 9-phenylfluorene with benzaldehyde have shown[12,13] that the relative thermodynamic stability of the adduct, phenyl(9-phenyl-9-fluorenyl)alkoxide (II), diminishes simultaneously with increase of the radius of the metal atom and with increase of the polarity of the medium:



(4)

(II)

In dimethoxyethane (DME), the yield of compound (II) diminishes in the sequence Li ≅ Na > K > Cs and on passing from solvents of the ethereal type to dipolar aprotic solvents. In HMP the decomposition of compound (II) into the initial reactants takes place regardless of the size of the metal atom. HMP destabilises not only compounds (I) and (II) but also the lithium and caesium alkoxides formed[14,15] in reaction (5) of alkali metal salts of diphenylacetonitrile, 1,3-diphenylindene, 9-methoxycarbonylfluorene, and fluoradene with benzaldehyde. In DME in the presence of 3–4 mole % HMP, the yield of RPhCHOM does not exceed 5%:[15]

$$PhCHO + RM \overset{K}{\rightleftarrows} RPhCHOM. \qquad (5)$$

As a result of the possibility of the spectroscopic measurement of the concentration of the alkali metal salt of the CH acid at any stage of its reaction with benzaldehyde, in particular when the reaction system attains the equilibrium position, measurements were made for the first time[14–16] of the equilibrium constant *K* and a study was made of the factors influencing this quantity. In the reaction of alkali metal salts of 9-phenylfluorene with benzaldehyde in DME, the equilibrium constant decreases monotonically with increase of the HMP concentration. For the lithium salt, *K* = 208, 25, and 6 litre mol^{-1} at HMP concentrations of 5.6, 8.2 and 10.7 vol.% and for the sodium salt the constant is 39.6, and 0.7 litre mol^{-1} at HMP concentrations of 1.4, 3.5, and 10.7 vol.%. In conformity with the results of qualitative observations,[4–10] *K*(Li) > *K*(Na) in the reaction medium of the same composition (10.7 vol.% HMP), which is associated with the greater thermodynamic stability of the lithium alkoxides.

Table 1. The equilibrium constants for the reactions[14–16] of alkali metal salts with benzaldehyde in DME at 25 °C.

CH acid (RH)	pK_a[a]	*K*, litre mol^{-1} ($c = 10^{-4}$ M)		
		Li^+	K^+	Cs^+
9-Benzylfluorene	22.0	—	—	>100
1-Methyl-3-phenylindene	—	—	—	38
Ethyl diphenylacetate	22.4	—	—	29
Diphenylacetonitrile	17.8	23	15	22
9-Phenylfluorene	18.5	—	14	15
1,3-Diphenylindene	12.8	16	—	2.4
Fluoradene	10.5	7.2	2.8	2.2
9-Methoxycarbonylfluorene	10.4	1.8	—	0.25
9-Cyanofluorene	8.5	—	—	0.32

[a] The pK_a were taken from Petrov et al.[17]

Measurements of the equilibrium constant have also been performed[14–16] in DME for the reactions of benzaldehyde with alkali metal salts of CH acids of different structure, whose pK_a were varied within the range of approximately 14 units (Table 1). The common features in the variation of the equilibrium constant are then as follows: (1) the increase of *K* with decrease of the thermodynamic stability of the reacting carbanion (in the presence of a fixed

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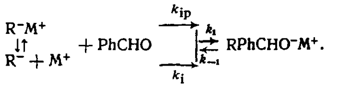
†The main reaction pathway in HMP is enolisation, which will be examined in detail in the next Section of the review.

cation) whose measure is the pK_a of the conjugate CH acid and (2) the decrease of K with increase of the radius of the alkali metal cation (for a fixed CH acid). The variation of K in the sequence Li > K > Cs agrees with the results of the study of the thermodynamic stability of alkali metal alkoxides of different structure.[4-10] At the same time, the shift of equilibrium (5) towards the initial reactants with increase of the thermodynamic stability of the carbanion is a fact which is difficult to justify without rigorous quantitative measurements, although intuitively it appears to be fairly natural.

On the basis of the results of studies of equilibrium (5), an energetic approach has been developed[13,15] to the determination of the relative thermodynamic stability of the adducts. In this approach, account is taken of the fact that the alkali metal salts of CH and OH acids are ionic compounds and that they exist in solution in the form of an equilibrium mixture of free carbanions, ion pairs, and even (in the case of alkali metal alkoxides) associated species made up of ion pairs. One of the main factors influencing the position of equilibrium (5) is the energy of the interaction of the charged fragments of the ion pair $RPhCHO^-M^+$: the smaller this energy, the lower the value of K. The interaction energy diminishes with increase of the radius of the cation and of the degree of its solvation (in the presence of HMP and crown polyethers[13])—the equilibrium constant diminishes correspondingly. It is of interest that calculation for the gas phase[18] demonstrates a clear decrease of the C–H bond energy in alkali metal methoxides $H{-}CH_2OM$ on passing from Na (333 kJ mol^{-1}) to K (326 kJ mol^{-1}); the energy of the C–H bond is even lower in the free methoxide anion (306 kJ mol^{-1}). Presumably the interaction in the ion pair–O^-M^+ influences analogously the C–R bond energy in the alkali metal alkoxides $\rangle C(OM){-}R$.

The study of the kinetics of the reactions of alkali metal salts of CH acids with benzaldehyde in DME established[14-16] that both free carbanions (rate constant k_i) and ion pairs (rate constant k_ip) participate in the stage involving addition to the carbonyl group:

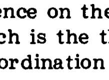


$$\left.\begin{matrix} R^-M^+ \\ \downarrow\uparrow \\ R^- + M^+ \end{matrix}\right. + PhCHO \begin{matrix} \xrightarrow{k_\mathrm{ip}} \\ \\ \xrightarrow[k_\mathrm{i}]{} \end{matrix} \Big| \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} RPhCHO^-M^+. \tag{6}$$

Since two types of ionic species participate in the reaction and the reactivity of the free carbanions is appreciably higher than that of the ion pairs, the observed reaction rate constant k_1 depends on the concentration of the alkali metal salts of the CH acid in a fairly complex manner. At the same time the reverse reaction (k_{-1}) takes place only with participation of complex ion pairs $RPhCHO^-M^+$ and the observed rate constant is independent of the concentrations of the reactants.

The features characterising the changes in the rate constants k_i and k_ip (Table 2) as a function of the radius of the alkali metal cation and the structure of the carbanion resemble those observed in nucleophilic aliphatic substitution reactions[19] with participation of alkali metal salts of CH acids. However, there are also significant differences. A common feature is the higher reactivity of free carbanions regardless of the variation of other factors, i.e. $k_\mathrm{i} > k_\mathrm{ip}$. Since in virtually all cases (with the exception of the lithio-derivatives of 1,3-diphenylindene and fluoradene)[19,20] the ion pairs of the alkali metal salts investigated are of the contact type, k_i exceeds k_ip approximately by two orders of magnitude. In a reaction system with solvate-separated ion pairs (1,3-diphenylindenyl-lithium), $k_\mathrm{i}/k_\mathrm{ip}$ is appreciably lower (~13).

A new factor, which was not encountered previously in the reactions of alkali metal salts of CH acids, is the dependence of the rate constant for the reaction of the free carbanion on the radius of the alkali metal caton when lithium and caesium salts are compared. In the case of alkali metal derivatives of diphenylacetonitrile, 1,3-diphenylindene, and fluoradene, $k_\mathrm{i}(Li^+)$ exceeds $k_\mathrm{i}(Cs^+)$ by a factor of 6–15, while for the reactions of alkali metal salts of 9-methoxycarbonylfluorene the difference between $k_\mathrm{i}(Li^+)$ and $k_\mathrm{i}(Cs^+)$ approaches two orders of magnitude. In order to account for this result,[14,15] one can invoke the idea, put forward by Lefour and Loupy,[1] that the carbonyl group is activated by the formation of a complex between the Li^+ cation and the oxygen atom:



Complex formation entails an increase in the electrophilicity of the carbonyl group, because there is an increase[1,21] in the positive charge on the carbon atom and a decrease of the LUMO energy. According to calculated data in two communications,[1,21] the formation of complexes between Li^+ and acroleine, benzaldehyde, acetophenone, and aliphatic aldehydes in the gas phase results in a decrease of the LUMO energy in these carbonyl compounds by 600–700 kJ mol^{-1}. Since there are experimental facts[21] indicating the possibility of controlling the reactions of carbonyl compounds and organic derivatives of alkali metals by means of the LUMO and HOMO energies, these calculations merit special attention. While coordination to Li^+ lowers[1] the energy of the LUMO of acroleine by 695 kJ mol^{-1}, coordination to Na^+ alters the LUMO energy by 454 kJ mol^{-1}. Large cations, for example Cs^+, have little influence on the LUMO energy of the carbonyl compound. Such is the theoretical assessment of the possibilities of the coordination of the cation to the carbonyl group.

Table 2. The rate constants[a] for the reactions involving the addition[15,16] of the free carbanions (k_i) and their ion pairs (k_ip) to the carbonyl group of benzaldehyde in DME at 25 °C.

CH acid	M^+	10^3k_i	10^5k_ip
9-Methylfluorene	Cs^+	310	840
Diphenyl(2-pyridyl)methane	Cs^+	170	570
Diphenylacetonitrile	Li^+	203	224
"	Cs^+	13.5	24.7
1,3-Diphenylindene	Li^+	8.8	66
"	Cs^+	0.85	0.34
Fluoradene	Li^+	4.66	—
"	Cs^+	0.83	1.33
9-Methoxycarbonylfluorene	Li^+	22.8	2.26
"	Cs^+	0.32	0.52
9-Cyanofluorene	Cs^+	0.14	0.24

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[a] The dimensions of the constants are litre mol^{-1} s^{-1}.

Experimental data have confirmed[22-25] the possibility of the formation of complexes of Li^+ with aldehydes and ketones. However, these data have been obtained in studies in solutions in the carbonyl compounds themselves,[22] in acetonitrile,[23,24] and in aqueous alcoholic mixtures.[25] On the other hand, when one is dealing with the coordination of an alkali metal cation to the carbonyl group in solvents of the ethereal type, many questions arise. Firstly, there are no convincing thermodynamic data in support of such coordination. It is known that the basicity of ethereal solvents is as a rule higher than the basicity of carbonyl compounds. For example, the Kamlet–Taft basicity parameters B_{CT} [26] for acetone and cyclohexanone are respectively 0.37 and 0.41, while the values for ether and THF are respectively 0.49 and 0.47. The change in ΔH on formation of a complex between Li^+ and THF, DME, and glymes by 0.3–20 kJ mol^{-1} in absolute magnitude exceeds the corresponding parameter for the reaction of Li^+ with acetone.[27] Admittedly there are data[28] showing that the energies of the complex formation reactions of Li^+ with ether, formaldehyde, and acetaldehyde are similar: −163, −149, and −169 kJ mol^{-1} respectively.

Secondly, in the reaction medium the concentration of the carbonyl compound is usually lower by one–two orders of magnitude than the concentration of the ethereal solvent. Thus, even if the complex of the alkali metal cation with the carbonyl group is formed, its concentration should probably be small and should depend greatly on the reaction conditions.

At the present time the concept[1] of the formation of a complex of the alkali metal cation with the carbonyl group is widely used[21,29–35] also in the interpretation of the results of studies on reactions of lithio-derivatives with aldehydes and ketones. One can therefore mention also data obtained in the investigation of related systems. The fluoradenyl anion[36] and carbanions of the benzyl type[37] react with epoxyethane more slowly than their lithium ion pair because, according to the authors' hypothesis, the cation forming part of the composition of the ion pair cooperates with the opening of the epoxide ring by being coordinated to the oxygen atom.

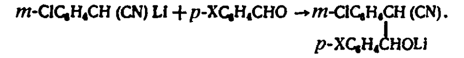
Among the results obtained[16] in the study of the kinetics of the reactions of alkali metal salts of CH acids with benzaldehyde, yet another experimental fact is of great interest. The rate constants for the addition of the carbanions (k_i) and their caesium ion pairs (k_{ip}) to the carbonyl group vary in parallel with the rate constants for the reactions of the same species in nucleophilic aliphatic substitution processes. Furthermore, the logarithms of the nucleophilic addition and nucleophilic substitution rate constants are linearly related. This shows that the nucleophilic properties of the ionic species determine their reactivity in both processes.

Interesting effects of the medium and the cation have been observed[29] in the reactions of alkali metal derivatives of nitriles with benzaldehyde and its *para*-substituted derivatives. The yield of the adducts (III) in reaction (7) does not depend greatly on the size of the metal atom—98% for Li, 70% for Na, and 80% for K, but it nevertheless reaches its maximum value in the reaction with the lithium salt:

$$\mathrm{MCH_2CN + PhCHO \rightarrow \underset{(III)}{PhCH(CH_2CN)OM}}. \qquad (7)$$

In the light of the foregoing examination of the interactions of alkali metal salts of CH acids with aldehydes, these data constitute indirect evidence for the reversibility of reaction (7), although the authors[29] make no mention of this important factor. Incidentally, if the equilibrium constants of reaction (7) are estimated by assuming that the initial reactant concentrations are 0.1 M,[29] then entirely reasonable values are obtained: 10^4 for Li, 80 for Na, and 200 litre mol^{-1} for K. Taking into account the fact that reaction (7) was carried out in THF and not in DME and at −80 °C and not at 25 °C (pK_a for acetonitrile is 24), the constants obtained agree fairly well with the data presented in Table 1. It is of interest that the variation of the equilibrium constant as a function of the cation ($Li^+ > K^+ > Na^+$) is of the same character both for the reactions of alkali metal salts of diphenylacetonitrile[15] and for the reactions of alkali metal salts of acetonitrile. Judging from the time required to complete reaction (7), its rate varies in the sequence Li > Na > K. This result (subject to the condition that both free carbanions and ion pairs or even associated species comprising ion pairs react in THF at an alkali metal salt concentration of 0.1 M) clearly indicate the involvement of the cation in the activation of the carbonyl group. This is confirmed by the decrease of the rate of reacton following the addition of cryptand 211 to the lithium salt of acetonitrile. However, the rate of reaction of KCH_2CN in the presence of cryptand 222 increases, which the authors[29] believe is also associated with the increase of the fraction of free carbanions. On the other hand, cryptand 221 does not influence the rate of reaction of $NaCH_2CN$, which the authors explained by the cancellation of two effects—on the one hand, the suppression of the activation of the carbonyl group and, on the other, the increase of the contribution of the reaction involving the more reactive free carbanions.

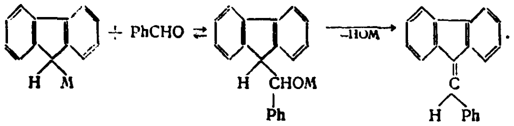
The half-life of the reaction of the lithium salt of *m*-chlorophenylacetonitrile with aromatic aldehydes in THF at −80 °C diminishes in the following sequence of X: CN (15 min) > H (10 min) > OCH_3 (5 min). When HMP is added, the sequence is reversed: CN (0.5 min) < H (2 min) < OCH_3 (45 min):



$$m\text{-}\mathrm{ClC_6H_4CH(CN)Li} + p\text{-}\mathrm{XC_6H_4CHO} \rightarrow m\text{-}\mathrm{ClC_6H_4}\underset{\substack{|\\ p\text{-}\mathrm{XC_6H_4CHOLi}}}{\mathrm{CH}}\mathrm{(CN)}. \qquad (8)$$

The rate of reaction of anisaldehyde diminishes, while other aldehydes react faster. The authors have interpreted these results[29] from the standpoint of the positions of the energy levels of the LUMO of the aldehyde relative to the HOMO of the carbanion assuming that, by virtue of the coordination of Li^+ to the carbonyl group, in THF the energies of the LUMO of all three aldehydes are equalised and are lower than the energies of the corresponding LUMO in a THF–HMP mixture, where such coordination does not occur.

The study of the reactions of alkali metal salts of fluorene with benzaldehyde under different conditions yielded[12,13] data concerning the influence of the solvent and the cation not only on the stage involving the addition of the nucleophile to the carbonyl group but also on the next stage in which a molecule of the alkali is eliminated, i.e. on the process modelling the crotonic condensation. In contrast to their 9-substituted derivatives, the unsubstituted fluorenyl salts [cf.Eqn.(4)] react with benzaldehyde in accordance with the following scheme:

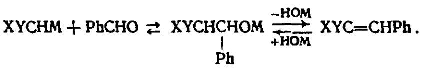


(IV) (V) (9)

The conversion of fluorenyl-lithium or fluoroenylsodium into the reaction products in ether and DME at concentrations of organic derivatives of alkali metals in the range 0.01–0.1 M and those of benzaldehyde in the range 0.03–0.4 M takes place over a period shorter than 1 s. The lithium and sodium salts of fluorene in HMP or its potassium, caesium and tetra-n-butylammonium salts in any of the solvents employed (ether, DME, HMP) react appreciably more slowly. Under these conditions, the complete consumption of the carbanion requires about 1 min. The retardation of the reactions in ether and DME in the presence of K^+, Cs^+, and Bu_4N^+ compared with Li^+ and Na^+ or the retardation of the reactions of fluorenyl-lithium and fluorenylsodium on passing to HMP (or after the introduction of solvating additives of the type of crown polyethers) is due to the appreciable shift of the equilibrium in the first stage of reaction (9) towards the initial reactants. In HMP or in the presence of large cations in ether and DME, the reactions considered in essence occur generally only because of the irreversible alkali elimination stage. For this reason, the only observed reaction product under these conditions is benzylidenefluorene (V).

In other cases the composition of the products depends on the competition between the first and second stages. A common feature is the increase in the yield of benzylidenefluorene with increase of the basicity (or with decrease of the thermodynamic stability) of the alkali metal alkoxide formed. The yield of benzylidenefluorine increases with increase of the polarity of the medium in the presence of the given cation (benzene < ether < DME < HMP in the presence of Li^+ and Na^+) and with increase of the radius of the cation in the given solvent. In DME: Li^+ (9%) < Na^+ (77%) < K^+, Cs^+, Bu_4N^+ (100%); in ether: Li^+ (16%) < Na^+ (70%) ≅ K^+ (69%); in benzene: Li^+ (0%) < Na^+ (23%) < Cs^+ (42%).

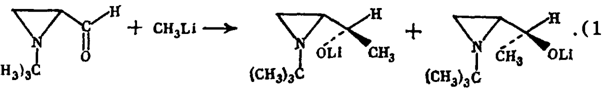
Whereas the elimination stage is irreversible in the reactions of alkali metal salts of fluorene and benzaldehyde, both stages are reversible in the Knoevenagel condensation [reaction (10)], where X and Y = CN or COOR:



$$XYCHM + PhCHO \rightleftarrows \underset{\displaystyle Ph}{XYCHCHOM} \underset{+HOM}{\overset{-HOM}{\rightleftarrows}} XYC{=}CHPh. \qquad (10)$$

For this reason, situations where both equilibria are fully displaced towards the initial reactants and the condensation product is not formed are entirely realistic. An example may be provided by the reaction[40] of sodiomalonic ester with benzaldehyde in ethanol. The condensation of $XYCH_2$ with carbonyl compounds is known to occur when amines are used as catalysts.[38,39]

Interesting results, which may indicate the coordination of the Li^+ cation to two heteroatoms of the carbonyl compound, have been obtained in a study of the reaction[31] of methyl-lithium with N-t-butyl-2-formylaziridine:

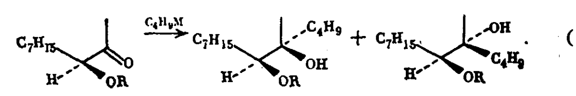


(11)

(VI) (VII)

A mixture of the stereoisomers (VI) and (VII), in which (VI) predominates (60%), is formed in THF. When LiBr is introduced into the reaction medium, at a concentration five times greater than that of methyl-lithium, the fraction of the isomer (VI) increases to 80%. The authors believe that the reaction proceeds via the formation of an intermediate complex from which the isomer (VI) should be formed with a higher probability.

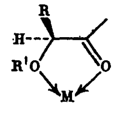
The coordination of the cation to oxygen ensures a high stereoselectivity also when organolithium and organomagnesium compounds interact with α-alkoxyaldehydes:[41,42]



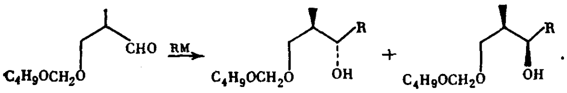
(12)

(VIII) (IX)

In reaction (12), which was carried out at −78 °C, the change in the nature of the solvent (n-hexane, chloroform, ether, THF) has little effect[42] on the ratio of the isomeric *threo*-product (VIII) and the *erythro*-product (IX): if M = Li and R = $CH_2OC_2H_4OCH_3$, the ratio (VIII)/(IX) varies from 3 to 0.7 (the smallest amount of the *threo*-isomer is formed in THF). If M = MgBr, the ratio (VIII)/(IX) increases to 9–14 in hexane, ether, and chloroform, and exceeds 100 in THF. The same high stereoselectivity [(VIII)/(IX) = 100 to 200] is observed[42] in THF in the analogous reaction of the organomagnesium compound if R = methoxymethyl, methylthiomethyl, benzyl, benzyloxymethyl, and furfurylmethyl. The authors suggest[42] that reaction (12) proceeds via the formation of an α-chelate (five-membered coordination complex), which is more stable for magnesium than for lithium.



α-Chelation is weakly manifested[41] in reactions (ether, −78 °C) of methyl-, vinyl-, and n-butyl-lithium and methylmagnesium bromide with β-alkoxyaldehyde:

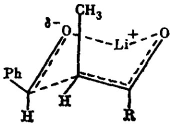


(13)

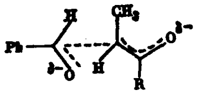
(X) (XI)

The ratio of the *threo*- and *erythro*-isomers formed (X)/(XI) varies in this instance only from 0.7 to 1.7. However, when lithium dimethyl- or di-n-butyl-cuprates are used in the reaction, the ratio (X)/(XI) increases respectively to 30 and 17. This ratio remains fairly high (12–20) also when the $C_4H_9OCH_2OCH_2$ group is replaced by $PhCH_2OCH_2$, $\overline{O(CH_2)_4C}HCH_2$, or $\overline{O(CH_2)_2OC}HCH_2$. It has been suggested[41] that the high stereoselectivity of the reactions of organocuprates with β-alkoxyaldehydes is due to β-chelation, i.e. the formation of an intermediate six-membered coordination complex. At the same time the stereoselectivity of the reactions of organocuprates with α-alkoxyaldehydes [for example, $PhCH_2OCH_2OCH(CH_3)CHO$] is low.[41] Unfortunately the nature of the distinct tendency of Grignard reagents towards α-chelation and of cuprates towards β-chelation in these reactions has not yet been established, although the excellent preparative possibilities associated with these effects are evident.

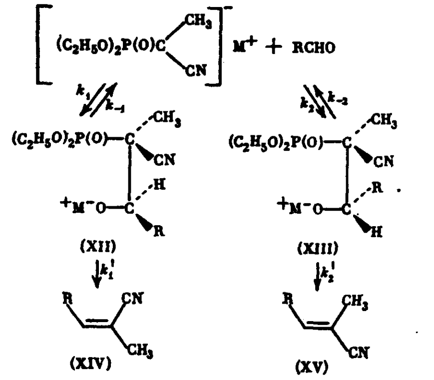
The *erythro*-aldol is formed exclusively[43] in the reaction of benzaldehyde with the lithium enolate of t-butyl ethyl ketone, while in the case of the lithium enolate of ethyl mesityl ketone, 92% of the *threo*-aldol and only 8% of the *erythro*-aldol is formed. The stereoselectivity of the first reaction does not change when HMP is introduced into the reaction medium, which the authors believe to be caused[43] by the formation of a six-membered transition state in which Li^+ is strongly bound to two oxygen atoms:



On the other hand, the use of the tetra-alkylammonium enolate of t-butyl ethyl ketone in this reaction is accompanied by the exclusive formation of the *threo*-aldol, which thus leads to the complete reversal of the stereoselectivity compared with the reaction in the presence of Li^+. In this case there is no possibility of the coordination of the cation to the oxygen atoms and they are thus both arranged in the transition state in such a way that the electrostatic repulsion between them is minimal:[43]



The conditions of the Horner–Emmons reaction also have an appreciable influence on the composition of the products formed (Table 3):[44,45]



(14)

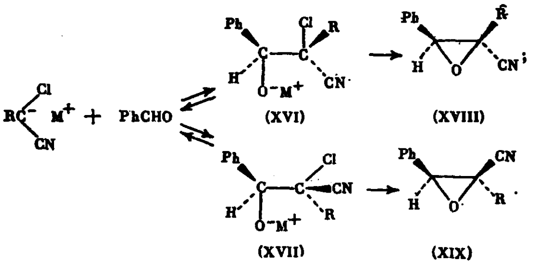
Table 3. The composition of the products of reaction (14) in THF as a function of temperature and the size of the alkali metal cation.[44,45]

R	t, °C	Li⁺			Na⁺			K⁺		
		$(XIV)^a/(XV)$	$(XIV)^b/(XV)$	k_{-1}/k_1'	$(XIV)^a/(XV)$	$(XIV)^b/(XV)$	$(XIV)^c/(XV)$	$(XIV)^a/(XV)$	$(XIV)^b/(XV)$	k_{-1}/k_1'
Ph	−78	0.43	3.0	0.6	1.0	—	—	9.0	19	1
	20	0.33	0.43	13	0.66^d	4^e	0.03^f	1.5	—	—
	65	0.25	0.33	15	0.54	—	—	1.0	1.5	4
p-$CH_3OC_6H_4$	−78	0.25	1.5	1	0.43	—	—	2.33	9.0	0.5
	20	0.25	—	—	0.43	—	—	1.5	—	—
	65	0.33	0.33	>40	0.64	—	—	1.02	1.02	>40

Remarks. Procedure followed in carrying out the reactions: [a]by mixing the initial reactants; [b]by starting with compound (XII): [c]by starting with compound (XIII); the ratios (XIV)/(XV) in HMP are [d]0.25, [e]16, and [f]0.02.

The aldol condensation stage in reaction (14) is reversible. For this reason, the product (XV) is formed, as shown by the authors,[44,45] not only on mixing the initial reactants but also when compound (XII), obtained by an independent procedure, is maintained in solution in THF or HMP (Table 3). Similarly, compound (XIV) can be obtained when compound (XIII) is kept in HMP or THF. The possibility of carrying out the experiment with compound (XII) or (XIII) obtained beforehand determines to a large extent the ratio of compounds (XIV) and (XV) formed ultimately. At low temperatures the decomposition of the alkoxides (XII) and (XIII) into the initial reactants (k_{-1}, k_{-2}) is relatively slow and this is why compounds (XIV) and (XV) are formed preferentially from compounds (XII) and (XIII) respectively. At high temperatures, the equilibration process is rapid (k_{-1}/k_1' and k_{-2}/k_2' are large), so that the product ratio (XIV)/(XV) is almost independent of the way in which the experiment is carried out (Table 3).

The epoxynitriles (XVIII) and (XIX) are formed in reaction (15) also via the reversible stage involving nucleophilic addition to the carbonyl group:[46]

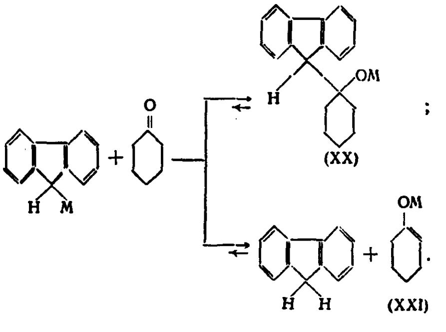


(15)

When a 1:1 mixture of compounds (XVII) and (XVI) synthesised beforehand is kept in HMP (Na⁺), benzene (Na⁺ and Li⁺), and THF (K⁺ and Li⁺), the ratio of the products formed (XIX)/(XVIII) is respectively >98, 0.43, 4.4, and 9. If PhCHO and RC(CN)(Cl)M are mixed, then compound (XIX) predominates among the products of reaction (15): the ratio (XIX)/(XVIII) exceeds 98 for Li⁺ in THF and benzene, while for Na⁺ in HMP and THF and for K⁺ in THF the ratio (XIX)/(XVIII) is respectively >98, 4, and 4. The only exception is the reaction of the sodium salt in benzene for which (XIX)/(XVII) is 0.18.

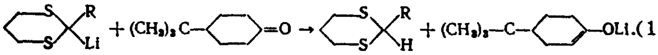
III. REACTIONS OF ORGANIC DERIVATIVES OF ALKALI METALS WITH KETONES

The reactions of organic derivatives of alkali and alkaline earth metals with ketones having a fairly mobile proton can lead to the formation[2] of both an adduct and an enolisation product. In this case detailed studies of the effects of the medium and the cation have been performed[12,47,48] in relation to the reactions of alkali metal salts of fluorene with cyclohexanone via the mechanism



(16)

In all the solvents investigated, the yield of the adduct (XX) increases with decrease of the radius of the cation. In DME: Bu_4N^+, Cs⁺, K⁺ (0%) < Na⁺ (5%) < Li⁺ (13%); in ether: Cs⁺ (0%) < Na⁺ (27%) < Li⁺ (72%); in benzene: Cs⁺ (7%) < Na⁺ (33%) < Li⁺ (80%). On the other hand, the yield of compound (XX) in the reactions of all the alkali metal salts investigated increases on passing to non-polar non-solvating media. HMP (0%) < DME (15%) < ether (72%) < benzene (80%) for Li⁺, DME (5%) < ether (27%) < benzene (33%) for Na⁺, and HMP, DME (0%) ≈ ether (0%) < benzene (7%) for Cs⁺. In HME the equilibrium is fully displaced towards the initial reactants. On the other hand, in the reaction of 2-lithio-1,3-dithiane and 2-lithio-2-phenyl-1,3-dithiane with 4-*t*-butylcyclohexanone, HMP has a somewhat different influence. In this solvent, the adduct (I) is not formed[11] and enolisation takes place instead:


(17)

Thus the enolate is not formed in the reaction of fluorenyllithium with cyclohexanone in HMP,[47,48] but enolisation does occur in reaction (17) in the same solvent. This apparent contradiction can be readily accounted for if one turns to the results obtained[49] in a study of the basicity of alkali metal enolates of cyclohexanone (and also cyclopentanone, ethyl methyl ketone, and acetophenone). In the presence of cryptands, the lithium, sodium, and potassium enolates of cyclohexanone ($pK_a = 18$) [50] metallate quantitatively triphenylmethane ($pK_a = 31.5$) [51] and diphenylmethane ($pK_a = 33$) [51] in THF, which is itself surprising merely on the basis of a comparison of the above pK_a for these compounds. The sharp increase of the basicity of the alkali metal enolates of cyclohexanone is caused by the fact that, in the presence of cryptands, they probably exist in the form of solvate-separated ion pairs (or even partly in the form of free enolate ions).

Thus it has been found that HMP, whose action is analogous to that of cryptands, increases the basicity of alkali metal enolates of cyclohexanone so much that they metallate quantitatively fluorene ($pK_a = 23$), fully displacing to the left the transprotonation equilibrium in scheme (16) (as well as the addition equilibrium). On the other hand, the pK_a for 1,3-dithianes are probably sufficiently high for enolisation in accordance with scheme (17). It is significant that enolisation does not occur in the reactions of alkali metal salts of fluorene with cyclohexanone also in DME[47,48] when the cations are K^+, Cs^+, or $(C_4H_9)_4N^+$. This shows that the basicity of the enolates increases also with increase of the radius of the cation.

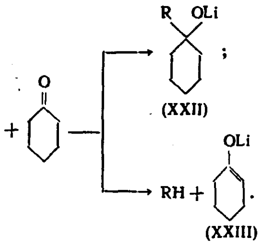
The yield of the adduct in the reactions of alkali metal salts of fluorene with cyclohexanone depends on the presence[47,48] of added inorganic lithium salts in the reaction system. Thus the yield of compound (XX) in the reaction of fluorenyllithium increases from 13 to 30% as a result of the introduction of $LiClO_4$ into DME. The yield of the product of the addition of propynyl-lithium to cyclohexanone or cyclopentanone increases analogously[52] to 80–90% under the influence of LiBr (in the absence of the salt, the yield varies in the range 40 to 60%).

LiBr exerts an unusual influence on the reaction of fluorenylpotassium and fluorenylcaesium with cyclohexanone in DME. The addition of this salt leads[48] to the instantaneous consumption of the carbanion but only the alkali metal enolate is formed in this process. The observed effect is probably determined in the first place by the occurrence of the exchange reaction[53,54]

$$RM + LiX \rightleftarrows RLi + MX. \qquad (18)$$

However, the absence of an adduct[48] suggests that LiBr activates not only the carbonyl group but also the α-CH bond of the ketone. On the other hand, the activated ketone enters preferentially into the enolisation reaction in this instance. This result agrees in general with the observed behaviour in the reactions of alkali metal salts of fluorene with cyclohexanone in DME: the yield of alkoxides in these reactions is always lower than that of the enolates.[47,48]

The interaction of alkyl organolithium compounds with cyclohexanone in ether or DME takes place[30,31] in accordance with scheme (19) which is analogous to scheme (16):



(19)

However, by virtue of the low CH acidity of RH ($pK_a > 40$) [55] and the high basicity of RLi, in this case both reaction pathways are apparently almost irreversible. The composition of the product is in this instance strongly influenced[30,31] by ionic and solvating additives. When cyclohexanone interacts with n-butyl-lithium, t-butyl-lithium, and ethynyl-lithium, the adducts (XXII) are formed rapidly in the first two instances and slowly in the last with a quantitative# yield.[30,31] In the presence of cryptand 211 in these reaction systems, enolisation takes place exclusively but, if apart from the cryptand, an equimolecular amount of LiBr is also introduced into the mixture, then compound (XXII) again becomes the only reaction product. In order to explain the results the authors used the concept of the activation of the carbonyl group by the formation of its complex with Li^+. The cryptand, which effectively binds Li^+, does not allow the cation to be coordinated to oxygen and LiBr plays the role of a donor of Li^+ ions capable of coordination.

A strong influence of the cryptand has been observed[30] also in a study of the reactions of n-butyl-lithium with the ethyl esters of benzoic, αα-dimethylpropionic, and α-methylpropionic acids. In ethereal solvents the alkyl-lithium compound adds to the carbonyl group while the addition of cryptand 211 fully inhibits the reaction and the initial esters can be isolated quantitatively from the reaction medium. Furthermore, it has been found[30] that cryptand 211 influences analogously also the reactions of alkyl-lithium compounds with carboxylic acids. In the presence of a large excess of n-butyl-lithium, it adds to the carbonyl group of benzoic, αα-dimethylpropionic, and α-methylpropionic acids (more precisely their lithium salts, which should be formed in the first stage). On the other hand, the cryptand precludes this addition owing to the absence, according to the authors,[30] of the coordination of Li^+ to the carbonyl oxygen atom.

The yield of the adduct can be increased[2] and that of the enolate decreased by lowering the reaction temperature. Whereas the addition of n-butyl-lithium to acetone, cyclohexanone, cyclopentanone, norcamphor, and acetophenone in ether at 0 °C proceeds respectively to the extent of 67, 82, 63, 76, and 73%, at −78 °C the respective yields are 80, 89, 75, 81, and 81%. Furthermore, it has been found that, in the reaction of t-butyl-lithium with various ketones, the yield of the adduct is lower (amounting to 50–70% depending on the structure of the ketone) than in the reaction with n-butyl-lithium and in the case of cyclohexanone it amounts to 53% (and not 100% as indicated by the studies of Perraud

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#According to Van Rijn et al.[52], the yield of the products of the addition of n-butyl-lithium to cyclohexanone usually does not exceed 80%.

and Handel[30,31]). The relative increase of the yield of the adduct with increasing temperature can probably be caused by two factors—the lower activation energy for the addition of the alkyl-lithium compound to the carbonyl group compared with the proton transfer reaction and/or the higher thermodynamic stability of the alkoxide compared with the enolate. It is noteworthy that the fraction of the adduct increases[47] with increase of temperature also in the reaction of fluorenyl-lithium with cyclohexanone in DME.

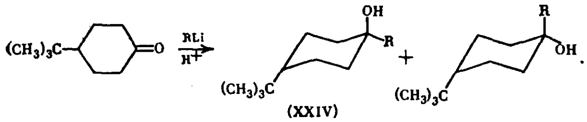
Analogously to the observations made[47,48] in the reactions of alkali metal salts of fluorene, an increase in the size of the cation lowers[2] the effectiveness of the addition reaction: t-butyl-lithium makes it possible to obtain 53% of 1-t-butyl-1-cyclohexanol, while t-butylsodium produces only 7% of this compound. According to O'Sullivan et al.[56], the yield of the adduct increases not only with decrease of the radius of the alkali metal cation but also on passing from organolithium, organosodium, and organopotassium derivatives to organomagnesium derivatives. In the reactions of a series of PhM with acetophenone, the ratio of the yield of the adduct to that of the enolisation product is 1:10 (hexane) for M = K, 1:1.4 (heptane) for M = Na, and 23:1 (ether) for M = Li. Enolisation does not occur at all when M = MgCl.[56]

In the synthesis of graft copolymers [in the reactions of polystyryl-lithium and polystyrylpotassium with poly(methyl methacrylate) and the copolymers of styrene with methyl vinyl ketone, acroleine, or methyl methacrylate], the degree of grafting (i.e. the fraction of the adduct) is always higher[57] when the reaction is carried out in non-polar media and not in THF and when the carbanion with the lithium counterion enters into the reaction with the carbonyl functional group. In the reaction of a carbanion of the benzyl type (the polystyryl anion) with 3-methyl-2-pentanone,[57] the yield of the adduct increases with decrease of the radius of the alkali metal cation (i.e. with increase of its affinity for oxygen) and on passing from THF to cyclohexane. Thus K^+ (20%) < Na^+ (50%) < Li^+ (73%) in THF and K^+ (48%) < Na^+ (59%) < Li^+ (79%) in cyclohexane. In this case too, the authors[57] believe that the addition is promoted by the coördination of Li^+ to the carbonyl group.

The addition of dimethylmagnesium to benzophenone has been investigated[58] in ether in the presence of various solvating additives. The authors established that dimethylmagnesium enters into the reaction in the form of 1:1 and 1:2 complexes with bidentate and monodentate solvating compounds respectively, the addition taking place without the elimination of ligands. Depending on the nature of the ligand, the reaction is accelerated (dimethyl ether, triethylamine, DME, HMP, β-methoxyethyldimethylamine) or retarded (THF, dioxan, tetramethylethylenediamine).

In the reactions of organomagnesium compounds with ketones, the composition of the products can be appreciably altered[59] by changing the nature of the medium, as happens in the case of organic derivatives of alkali metals. In the reaction of n-propylmagnesium bromide with diisopropyl ketone in ether, the ratio of the adduct and the reduction product is 37:63, increasing appreciably in benzene (to 64:36). An analogous situation has been observed in the reaction of n-propylmagnesium bromide with cyclohexyl isopropyl ketone (48:52 in ether and 86:14 in benzene) and with isopropyl propyl ketone (5:35 in ether and 13:61 in benzene). In the reaction with isopropyl propyl ketone, an appreciable amount of the enolisation product is also formed, its yield falling on passing from ether (60%) to benzene (26%).

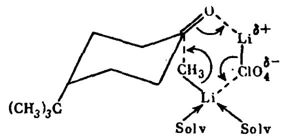
By varying the conditions in the reactions of organolithium compounds with 4-t-butylcyclohexanone [reaction (20)], it has been possible to alter,[60–62] albeit not within very wide limits, the ratio of the axial isomers (XXIV) and the equatorial isomers of the alcohols formed:



(XXIV)

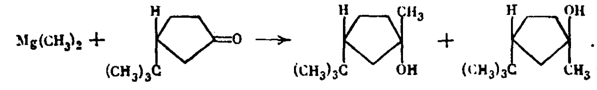
.(20)

In the reaction of methyl-lithium[61] in THF at −78 °C, the fraction of compound (XXIV) is 65–69%. The introduction of LiBr, LiI, $LiClO_4$, or $LiCu(CH_3)_2$ into the solution does not influence the yield of compound (XXIV). When the reaction is carried out in ether at −78 °C, the above additives make it possible to increase the fraction of compound (XXIV) to 87–92%.[61] The addition of $LiClO_4$ also increases somewhat[62] the yield of compound (XXIV) (from 58 to 69%) in the reaction of phenyl-lithium carried out under the same conditions. On the other hand, the increase of temperature from −78° to +5 °C lowers[60] the fraction of compound (XXIV)—for example, in the reaction of 4-t-butylcyclohexanone with n-butyl-lithium and s-butyl-lithium. The authors[60,61] believe that the influence of added inorganic lithium salts on temperature is manifested only when the reaction is performed in ether, because its complex forming effect does not greatly exceed the ability of the ketone to form a complex with Li^+. For this reason, in the reactions of a wide range of cyclic ketones with methyl-lithium in ether, the addition of lithium perchlorate should promote[62] the formation of a transition state from which only the axial isomer can be obtained.



It is noteworthy that it is very difficult to treat systematically the influence of the solvent on the stereoselectivity of the reactions of organolithium compounds with cyclic ketones, because each reaction system as a rule reacts in a fairly individual manner. In the reaction of ethynyl-lithium with 2-methylcyclohexanone,[63] the fraction of the axial alcohol is appreciably higher when the reaction is carried out in a non-polar solvent (benzene, 67%) than in THF (42%). The axial isomer is formed analogously in the reaction of ethylnyl-sodium[63] with a higher yield in benzene (53%) than in the polar THF–NH_3 mixture (41%). On the other hand, both in ether and in THF the product (XXIV) is formed[60] in virtually the same yield—69 and 65% respectively. In the reaction with 7-norbornene, n-butyl-lithium affords[64] 50% of the *endo*-isomer both in ether and in n-hexane. This is also true of the reaction of phenyl-lithium;[64] the yield of the *endo*-isomer is 72% in both solvents.

The solvent has an even weaker influence on the stereoselectivity of the reactions of organomagnesium compounds. In the reaction of dimethylmagnesium with 3-t-butylcyclopentanone, i.e.



(XXV)

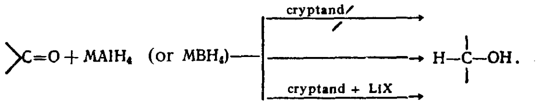
.(21)

the yield of the *cis*-isomer (XXV) is the same[65] in ether (53%), THF (52%), and anisole (54%). The yield of compound (XXV) is independent of the solvent (THF, anisole, ether); when methylmagnesium bromide reacts[65] with 3-t-butylcyclopentanone, the yield is again 53–54%.

The change of the cation in the reactions of organic derivatives of alkali metals with cyclic ketones has as a rule only a weak influence on the stereoselectivity, especially as the process takes place in a solvent which effectively solvates the alkali metal cations. The reaction of ethynyl-lithium and ethynylpotassium with 3-methylcyclohexanone in the THF–NH_3 mixture leads mainly to the equatorial isomer:[63] 82% (Li^+) and 80% (K^+). In the same medium but in the reaction of 2-methylcyclohexanone with $HC{\equiv}CM$ the yield of the equatorial isomer falls but a dependence on the cation cannot be observed:[63] 45% (Li^+), 41% (Na^+), and 44% (K^+). Only in benzene is the yield of the axial isomer somewhat higher[63] in the presence of Li^+ (67%) than in the presence of Na^+ (53%).

IV. THE HYDRIDE REDUCTION REACTIONS OF CARBONYL COMPOUNDS

Numerous studies[32–35,66–69] of the effects of the medium and the cation on the reduction of carbonyl compounds by alkali metal tetrahydroaluminates and tetrahydroborates have been published in recent years. The methodology of the majority of these investigations and their results are similar. They can be represented in the following form:

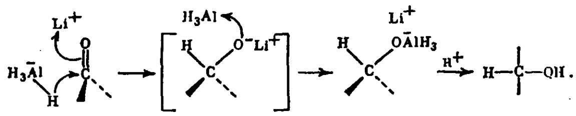


(22)

We shall examine initially the results obtained in the study of the reactions of alkali metal tetrahydroaluminates. In ethereal solvents (DME, THF, ether, diglyme), $MAlH_4$ (where M = Na or Li) reduces cyclohexanone,[32,33] 2-methylcyclohexanone,[66] 4-t-butylcyclohexanone,[66] cyclopentanone,[32] *N*-t-butylacetyl-2-aziridine,[35] α-chloropropiophenone,[67] benzaldehyde,[21] acetophenone,[21] p-methoxyacetophenone,[21] and compounds[32] having the general formula $C_2H_5C(O)X$, where X = H, OH, or C_2H_5, to the corresponding hydroxy-derivatives. In the present of cryptand 211 for M = Li and cryptand 221 for M = Na, hydroxycompounds are not formed[32,33,35,66,67] or, much more rarely,[21] the rate of their formation is sharply reduced. The rate of reduction is also lowered by the addition of crown ethers[68] and hexamethyltriethylenetetra-amine[34] but their effect is much weaker than that of cryptands.

Finally, if an inorganic lithium salt (LiBr, LiI, $LiClO_4$) [32,33,35] or sodium salt ($NaClO_4$) [33,35] is introduced into the reaction medium in addition to the cryptand, the effect of the latter is fully removed and quantitative reduction of the carbonyl compound is observed.

In order to account for the results, the idea of the activation of the carbonyl group as a result of the formation of a complex of the latter with an alkali metal cation has been used, as for the reactions involving organometallic compounds discussed above. For example, the reaction involving reduction by lithium tetrahydroaluminate has been described in this way:[33]



(23)

The reaction does not occur in the presence of cryptands, because the possibility of the formation of a complex between the alkali metal cation and the carbonyl group is then eliminated. On the other hand, if the reaction is carried out in the presence of equimolar amounts of lithium tetrahydroaluminate, the cryptand, and an inorganic lithium salt, then one equivalent of Li^+ ions not involving the complex remains for the activation of the carbonyl group.

It is surprising that no attention has been paid in any of the studies quoted to what may occur in the reaction mixture in the presence of the cryptand. After all the latter not only eliminates the possibility of the formation of a complex between the cation and the carbonyl group but in its presence there should be an appreciable increase of both the nucleophilicity and the basicity of the negatively charged tetrahydroaluminate fragment, which has been demonstrated by investigations of the reactions of organolithium compounds.[30,31] It is extremely likely that in the presence of cryptands $MAlH_4$ nevertheless reacts with ketones but via the transprotonation and not the addition mechanism, i.e. by enolising suitable carbonyl compounds. This has been confirmed indirectly by the finding that cyclohexanone is converted into the enolate under the influence of sodium, potassium, and lithium hydrides when cryptands are present in the reaction medium.[69] Yet another interesting question arises: is it possible to account for the influence of cryptands by the reversibility of the addition of the hydride to the carbonyl group? Although there is no experimental evidence in support of this claim, nevertheless this hypothesis is entirely reasonable.

The behaviour observed for the reactions of tetrahydroaluminates, discussed above, holds in general also for the reactions of alkali metal tetrahydroborates. Cryptands suppress the reduction of *N*-t-butylacetyl-2-aziridine,[35] cyclohexanone[33] and α-chloropropiophenone.[67] However, when $LiClO_4$ [33] or $NaClO_4$ [33,35] is introduced into the system together with the cryptand, the effect of the latter is removed. In contrast to $MAlH_4$, the reactions of MBH_4 can be carried out in hydroxylated solvents (water, alcohols) where the carbonyl group can be activated by the formation of hydrogen bonds with solvent molecules.[35,66,67,70] In methanol, *N*-t-butylacetyl-2-aziridine [35] is reduced rapidly by $NaBH_4$ regardless of whether the cryptand 221, $NaClO_4$, or $LiClO_4$ are present in the reaction medium. The addition of water to an ethereal solvent makes it possible to obtain the product of the addition of *N*-t-butylacetyl-2-aziridine,[35] α-chloropropiophenone,[67] 2-methylcyclohexanone,[66] and 4-t-butylcyclohexanone[66] even if the solvent contains the cryptand.

Lithium tetrahydroborate reacts faster with carbonyl componds than sodium tetrahydroborate, which has been observed in most varied solvents: pyridine,[71] isopropyl alcohol,[54,70] and water.[70] Thus $LiBH_4$ reduces ethyl benzoate in isopropyl alcohol, while $NaBH_4$ does not.[54] The rate constant for the reaction[70] of acetone with $LiBH_4$ in the same solvent (5×10^{-3} litre mol^{-1} s^{-1}) is almost three times as high as that for the reaction with $NaBH_4$ (1.5×10^{-3} litre mol^{-1} s^{-1}). However, in all cases this result is attributed to the more effective coordination of Li^+ (compared with Na^+) to the carbonyl group, which is sometimes believed[71] to be due to the higher nucleophilicity of the lithium ion pair (although without any special supporting evidence).

The importance of the activation of the carbonyl group is also indicated by data obtained in the study of the reduction of acetone[70] and esters[54] by tetrahydroborates. The reaction with $NaBH_4$ takes place only in water and alcohols and its rate increases with increase of the electron-donating capacity of the solvent: isopropyl alcohol < H_2O, ethanol. In acetonitrile, pyridine, DMF, and diglyme, $NaBH_4$ hardly reacts with acetone. Esters are not reduced by $NaBH_4$ [54] even in isopropyl alcohol. The addition of LiI and LiCl accelerates[70] the reduction of acetone by both $NaBH_4$ and

$LiBH_4$. In the presence of LiBr, ethyl acetate, ethyl stearate, ethyl benzoate, ethyl cinnamate, and ethyl *p*-chlorobenzoate begin to react with $NaBH_4$.[54] Here one must note that, whereas the acceleration of the reaction involving $LiBH_4$ can be accounted for solely by electrophilic catalysis, in the case of $NaBH_4$ inorganic lithium salts give rise to the possibility of cation exchange as well[54] [reaction (24)], so that subsequently the process can proceed with participation of $LiBH_4$:

$$NaBH_4 + LiX \rightleftarrows LiBH_4 + NaX. \qquad (24)$$

The reduction of esters by $NaBH_4$ can also be catalysed by $MgCl_2$ and $MgBr_2$.[54]

Contradictory data have been obtained concerning the catalytic role of amines. When acetone is reduced[70] by $LiBH_4$ and $NaBH_4$ in alcohols and diglyme, it is assumed that the latter do not affect the rate of reaction. On the other hand, under identical conditions (acetone in diglyme + $NaBH_4$) the acceleration of the reaction in the presence of the same triethylamine derivative has been observed.[54]

Among the communications[34,68,72] devoted to the investigation of the kinetics of the reduction of ketones by lithium and sodium tetrahydroaluminates, much attention has been devoted in the paper of Ashby et al.[72] to the investigation of the state of the tetrahydroaluminates in solution in THF. Measurements were made of the dissociation constants of $MAlH_4$ over a wide temperature range and the thermodynamic parameters of the dissociation reaction have been calculated. At 25 °C, $K_D = 6.9 \times 10^{-7}$, 2.1×10^{-7}, and 1.8×10^{-6} mol litre^{-1} for M = Li, Na, and Bu_4N respectively. The temperature dependence of the enthalpy and entropy of dissociation led to the conclusion[72] that the lithium ion pairs $MAlH_4$ are of the solvate-separated type, while the sodium ion pairs are mainly of the contact type.

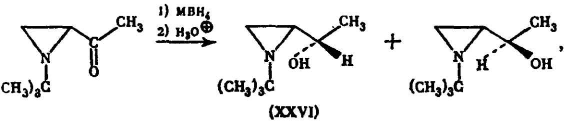
Ashby and Boone[34] used a second-order equation to describe the reactions involving the reduction of mesityl phenyl ketone by $LiAlH_4$ and $NaAlH_4$ in THF. However, this equation is inapplicable[20] if it is assumed[34] that the process takes place with participation of only the free ions or the free ions and the solvate-separated ion pairs.

At 25 °C the observed rate constant for the reaction of mesityl phenyl ketone with $LiAlH_4$ (0.595 litre mol^{-1} s^{-1}) is ten times greater than the rate constant for the reaction with $NaAlH_4$ (0.0587 litre mol^{-1} s^{-1}), which is caused, according to the authors,[34] by the effective activation of the carbonyl group by the lithium cation and not by the difference between the states of the above tetrahydroaluminates in solution. The activation parameters for the reaction of $LiAlH_4$ differ appreciably from the analogous parameters in the case of $NaAlH_4$: $\Delta H^{\neq} = 9.9$ and 17.5 kcal mol^{-1} respectively and $\Delta S^{\neq} = -26.2$ and -5.4 e.u. respectively, which is attributed[34] to the more intense interaction of the ketone with Li^+ in the activated complex.

Under the same conditions as for mesityl phenyl ketone, camphor was reduced[57] by $LiAlH_4$ and $NaAlH_4$. The reaction involving Li^+ is also much faster than that with Na^+, but its kinetic orders with respect to $LiAlH_4$ (1.0) and $NaAlH_4$ (0.73) are different. The authors explain this result by the dimerisation of $NaAlH_4$ (in their view lithium tetrahydroaluminate exists in the monomeric form in THF). However, one should note that the association of ion pairs usually intensifies[20] with decrease of the radius of the alkali metal cation. On the other hand, when the data of Ashby and Boone[34] are used, it is easy to explain the observed kinetic orders with respect to the tetrahydroaluminate. $LiAlH_4$ reacts in the form of free ions and solvate-separated ion pairs (these species usually have[19,20] comparable reactivities) and the order with respect to the tetrahydroaluminate should therefore be close to unity. $NaAlH_4$ is partly dissociated in THF [34] and reacts only in the form of H_4Al^-, so that the order with respect to this reactant should be fractional.[20]

In a study of the reduction of camphor by $LiAlH_4$, Wiegers and Smith[68] made a fairly strange observation: the reaction is retarded by both LiBr and crown polyether. In order to explain this finding, one may suppose that in this instance LiBr not only plays the role of the electrophilic catalyst but also suppresses the dissociation of $LiAlH_4$ via the common ion effect[20] and the latter effect is more important.

Data concerning the influence of the nature of the cation and the solvent on the stereochemistry of the reduction of carbonyl compounds have been obtained in a number of studies. The reaction of tetrahydroaluminates and tetrahydroborates with *N*-t-butylacetyl-2-aziridine, i.e.



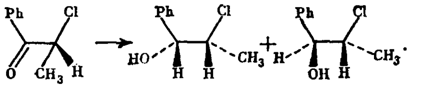
, (25)

(XXVI)

and the reaction of *N*-t-butyl-2-formylaziridine with methyllithium [cf.Eqn.(11)] result in the formation of two products.[35] In the absence of additives in diglyme, the product (XXVI) predominates (>98 and 92% in the reactions with $LiAlH_4$ and $LiBH_4$ and 80 and 70% in the reactions with $NaAlH_4$ and $NaBH_4$), which is due to the formation of a complex by the alkali metal cation with two heteroatoms of the substrate (see above). The yield of compound (XXVI) is greater in the case of Li^+ than Na^+, which is a consequence of the more effective complex formation with the cation having a smaller radius. In the presence of added cryptands and metal salts in diglyme, the stereochemical result is determined by the cation of the added salt, which indicates a high selectivity in the complex formation reaction of the cryptand. In the reaction involving $LiAlH_4$, together with cryptand 221 + NaI, the yield of compound (XXVI) is the same as in the reaction with $NaAlH_4$ in the absence of additives, while in the reaction with $NaBH_4$ + cryptand 221 + $LiClO_4$ the yield is the same as in the reaction with $LiBH_4$ in the absence of additives.

Since in the reduction of *N*-t-butylacetyl-2-aziridine by $NaBH_4$ in methanol the carbonyl group is activated not only by the alkali metal cation but also (no less effectively) by solvent molecules, the stereoselectivity of the reaction is low: the fraction of the product (XXVI) is about 40%.[35] Only in the presence of large amounts of $LiClO_4$ is it possible to increase the yield of compound (XXVI) to 90%.

The influence of the cation and the solvent on the stereoselectivity of the reduction of α-chloropropiophenone is not very pronounced:[67]



(XXVII)

The yield of compound (XXVII) increases with increase of the solvating capacity of the solvent (on passing from ether to DME) and in DME it diminishes only slightly with increase of the radius of the cation. In almost all cases the yield of compound (XXVII) under identical conditions is slightly higher in the reaction with $MAlH_4$ than in the reaction with MBH_4. The yield of compound (XXVII) is 72% ($LiAlH_4$) and 68% ($LiBH_4$) in ether, and 94% ($LiAlH_4$) and 91% ($LiBH_4$) in the presence of Li^+ and 90% ($NaAlH_4$) and 88% ($NaBH_4$) in the presence of Na^+ in DME. The stereoselectivity is almost the same in DME and methanol: in the reaction with $NaBH_4$, the yields of compound (XXVII) are respectively 88 and 85%. In both DME and methanol, the composition of the products is independent of the addition of inorganic solvents (LiBr, NaBr).

The reaction conditions, namely the variation of the solvent (ether, DME, methanol) and the cation (Li^+, Na^+) and the addition of LiBr, has the same weak influence on the stereochemistry of the reduction^{66} of 4-t-butylcyclohexanone and 2-methylcyclohexanone by alkali metal tetrahydroaluminates and tetrahydroborates. When the former ketone is reduced, the yield of the *cis*-isomer varies in the range 11 to 15%, while in the latter case it varies in the range 22–39%.

The stereochemistry of the reduction of carbonyl compounds has been examined in greater detail in Wigfield's review.^{73}

V. CONCLUSION

Analysis of the available literature data on the reactions of organic derivatives of alkali metals and alkali metal tetrahydroborates and tetrahydroaluminates with carbonyl compounds permits the perfectly definite conclusion that the rates of these reactions and the compositions of the products formed can be varied within wide limits by altering the nature of the medium and the metal atom. In certain cases the observed effects permit a quantitative treatment, but usually they can be understood only at a qualitative level, normally by resorting to the idea that the cation is coordinated to the carbonyl oxygen and other heteroatoms. Although the mechanisms of many of the processes investigated have not yet been elucidated in detail owing to the lack of sufficient quantitative data, nevertheless one can already speak of the existence of definite regularities, which may serve as a basis for the successful planning of preparative experiments. Thus it is quite evident that the stereoselectivity can be increased by lowering the polarity of the solvent and by decreasing the size of the alkali metal cation (sometimes by replacing organic derivatives of alkali metals by organomagnesium compounds). The thermodynamic stability of the adduct can be increased by the same procedures and hence its yield can be increased. On the other hand, in order to increase the rate of the nucleophilic addition of the organic derivative of the alkali metal, one must intensify the solvation of the cation, naturally without forgetting at the same time the important role of the cation in the activation of the carbonyl group.

One must assume that further studies on the reactions of organic derivatives of alkali metals with carbonyl compounds, carried out at an effective quantitative level, will permit the final formulation of the idea concerning the role of the various factors in these reactions and hence will make possible certain reliable predictions about the outcome of the process in each specific instance.

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The Cope Aza-rearrangement in Organic Synthesis

N.M.Przheval'skii and I.I.Grandberg

The latest advances in the application of the Cope aza-rearrangement in organic synthesis are examined and the results of studies on the mechanism of the reaction and of its use in syntheses are surveyed.
The bibliography includes 147 references.

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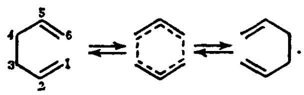
I. INTRODUCTION

Pericyclic reactions, including sigmatropic rearrangements, have attracted much attention by chemists in recent years.[1-3] In the first place this is because the [3, 3]sigmatropic shift, which embraces also the Cope rearrangement,[4] gives rise to a predictable regiostereoselectivity in the formation of new bonds.[5,6] No less important is also the fact that new approaches to the synthesis of a wide variety of heterocyclic and acyclic structures have been demonstrated and interesting stereochemical features of the rearrangement have been observed with the aid of this reaction.

In the present review we shall consider studies devoted to the theoretical and synthetic aspects of the Cope aza-rearrangement. Mainly studies carried out in 1978–1984, published after the review of Heimgartner et al.[7] which quotes the literature up to 1977 inclusive, are discussed. In certain instances earlier communications are invoked in order to preserve the integrity of the exposition.

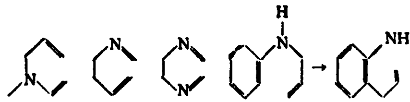
The thermal rearrangement of hexa-1,5-dienes (I), called the Cope rearrangement,[4] belongs to the class of [3, 3]sigmatropic processes[8] which proceed via the six-membered transition state (II):



(I) (II) (III)

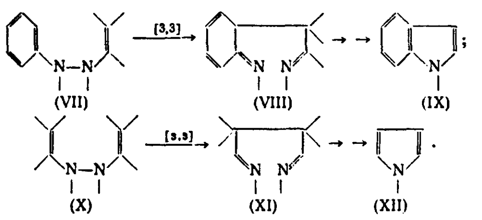
The replacement of one or several carbon atoms in the diene (I) by nitrogen leads to the corresponding aza-hexadiene systems (IVa–c), for the rearrangement of which the term the Cope aza-rearrangement has been proposed.[9]

When 3-azahexa-1,5-diene (V), in which one double bond is incorporated in an aromatic nucleus, undergoes the Cope rearrangement, then reactions of this type are frequently referred to as the Claisen (V) → (VI) amino-rearrangement.[10]



(IVa) (IVб) (IVв) (V) (VI)

On passing to 3,4-diazahexa-1,5-diene, systems of the type of the enehydrazine (VII) or dienehydrazine (X) are produced, whose rearrangement is a stage in the formation of the carbon—carbon bond in the Fischer indole synthesis[11,12] and the Piloty pyrrole synthesis:[13]



(VII) (VIII) (IX) (X) (XI) (XII)

The transformations (V) → (VI) and (VII) → (IX) can be regarded as the Cope 3-aza- and 3,4-diaza-rearrangements. A general classification of sigmatropic "Cope hetero-rearrangements" has been published.[14]

Apart from the reactions indicated, those involving systems of type (IV), containing heteroatoms (O, S) other than the nitrogen atom, i.e. the Cope oxaza- and thiaza-rearrangements, have been discussed.

The general postulates of the theory of sigmatropic rearrangements developed by Woodward and Hoffmann,[8] mainly for thermal non-catalytic reactions of hydrocarbons, were subsequently extended to both thermal and catalytic reactions of aliphatic and aromatic heterosystems.[15]

The following criteria were mainly used to assign these reactions to the concerted [3, 3]shift type: the first order of the reaction; the large negative activation entropies; comparatively small (by a factor of 20–30) changes in the rate after the introduction of electron-donating or electron-accepting substituents; the inversion of allyl groups; the retention of optical activity in the products when the initial molecule was optically active. The mechanism of the Cope 3-oxa-rearrangement of a series of allyl vinyl[17] and allyl aryl ethers[17] (the aliphatic and aromatic Claisen rearrangements), their thio-analogues,[18] (the Claisen thia-rearrangement), and the allyl esters of carboxylic acids,[19] for example, has been established with the aid of these criteria.

Numerous experimental data obtained in the course of these investigations demonstrated that the Cope rearrangements and the Cope hetero-rearrangements are much faster for charged or highly polarised systems.[1-3,7] Reactions of this type have been called charge-induced[20,21] and charge-accelerated[22] [3, 3]sigmatropic rearrangements.

The charge-induced reactions are in fact of greatest interest for the Cope aza-rearrangements, because they facilitate significantly the conditions under which they can be carried out and increase the yield of products.

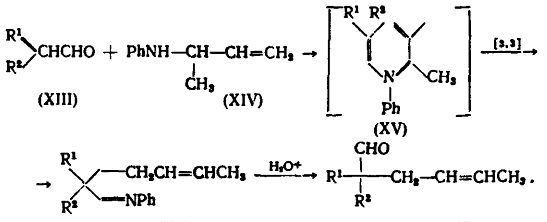
At the same time, as stated in a review,[7] the available information about the mechanism of these reactions is limited. Definite progress has been achieved in this respect only recently (see Sections II–VI).

II. THE COPE 3-AZA-REARRANGEMENT

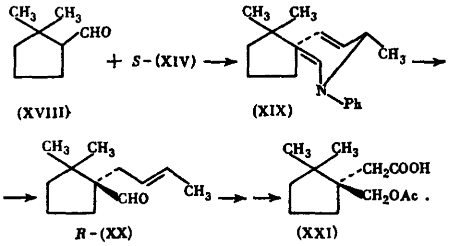
1. The Aliphatic Cope 3-Aza-rearrangement

One of the first examples of the aliphatic Cope 3-aza-rearrangement was described in a study[10] where it was shown that it proceeds via a transition state in the chair conformation. Since the thermal Cope 3-aza-rearrangement usually requires high temperatures, attempts have been made to achieve the reaction under mild conditions using Lewis acids,[23,24] sulphuric acid,[25] and $TiCl_4$ [26] as catalysts.

Thus the reaction of the aldehydes (XIII) with N-(1'methylallyl)-aniline (XIV) (benzene, $TiCl_4$) leads to the formation of the intermediate (XV) which rearranges to the imine (XVI), whose hydrolysis affords the aldehyde (XVII):



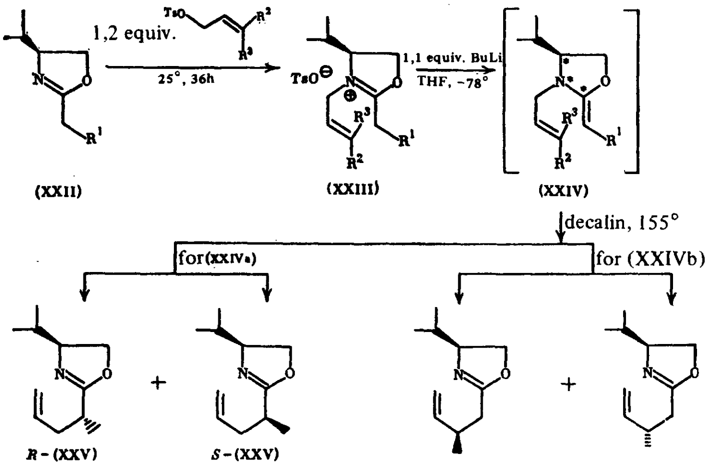
If the optically active amine S-(XIV) with $[\alpha]_D^{27} = 1.47°$ is introduced into the reaction with 2,2-dimethylcyclopentanaldehyde (XVIII), then the *trans*-aldehyde (XX) with $[\alpha]_D^{27} = -2.53°$ and having the R-configuration is formed via the intermediate S-(XIX):[26]



By reduction with sodium tetrahydroborate, acetylation, and oxidation with permanganate, compound (XX) was converted into the acid (XXI), which is an important intermediate in the synthesis of an optically active pheromone.[27]

One of the disadvantages of the above transformation (XV) → (XVII) is the necessity to employ optically pure allyl substrates in order to obtain optically pure products. Furthermore, the chirality in the initial optical centre is lost during the reaction. An attempt to overcome these difficulties has been made in a theoretically and synthetically important study[28] in which asymmetric induction was achieved in the Cope 3-aza-rearrangement by means of an auxiliary reagent. The authors began with the hypothesis that an auxiliary chiral centre bound covalently to the nitrogen atom would create a transition state bias in the Cope aza-rearrangement. In order to enhance to the maximum possible extent the topological influence of the auxiliary chiral reagent, this centre, the nitrogen atom, and the C(1) atom of the vinyl fragment (denoted by an asterisk) were incorporated in the five-membered oxazoline ring:

Scheme 1



(XXII) (XXIII) (XXIV)

R-(XXV) S-(XXV)

R-(XXV) : S-(XXV) = 87 : 13

(XXII)–(XXVI)

a) $R^1 = CH_3$, $R^2 = R^3 = H$

b) $R^2 = CH_3$, $R^1 = R^3 = H$

c) $R^3 = CH_3$, $R^1 = R^2 = H$

R-(XXVI) S-(XXVI)

R-(XXVI) : S-(XXVI) = 87 : 13 for XXIVb)

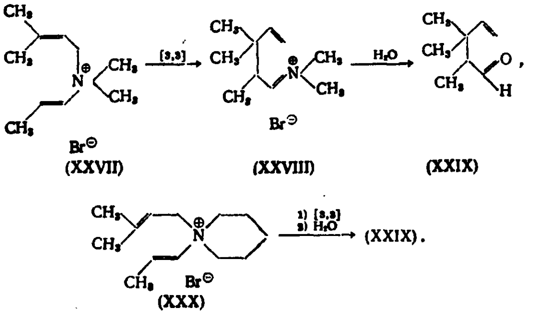
R-(XXVI) : S-(XXVI) = 14 : 86 for XXIVc)

The salts (XXIIIa–c) were obtained from the oxazolines (XXIIa–c) with the aid of allyl toluene-p-sulphonates. The neutralisation of the salts (XXIIIa–c) leads to the NO-acetals (XXIVa–c) which rearrange in decalin, without isolation, to the oxazolines (XXV) and (XXVI) in yields exceeding 85% (Scheme 1).

The diastereoselectivity of this Cope 3-aza-rearrangement was determined in the following manner. The oxazoline (XXV) was hydrolysed (3 N HCl 90 °C, 1.5 h) and the subsequent optical measurement showed that R-(−)-2-methylpent-4-enoic acid is formed in excess so that compound (XXIVa) rearranges predominantly to the oxazoline R-(XXV). The ratios of the diastereoisomeric oxazolines R-(XXV)/S-(XXV) and R-(XXVI)/S-(XXVI) were established by means of high-pressure liquid chromatography. Analysis of the high-resolution ^1H NMR spectra (500 MHz) of the N-methyl-oxazolinium salts obtained from compounds (XXV) and (XXVI) by methylation with dimethyl sulphate demonstrated that one of the diastereoisomers is present in 72–74% excess in the rearrangements (XXIVa) → R-(XXV), (XXIVb) → R-(XXVI), and (XXIVc) → S-(XXVI).

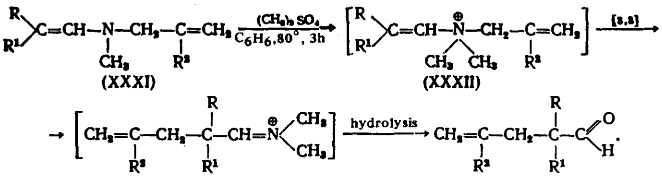
The rearrangement of the enammonium salt (XXVII) under mild conditions (20 °C) under the influence of bases has been described.[29] The hydrolysis of the resulting amine (XXVIII) leads to the aldehyde (XXIX):

Scheme 2



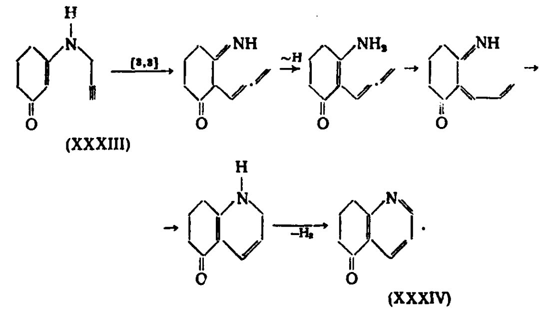
The aldehyde (XXIX) also arises as a result of the Cope 3-aza-rearrangement when a benzene solution of the bromo-derivative (XXX) is maintained at room temperature[29] (Scheme 2).

A promising method for the generation of the quaternary carbon centre under mild conditions with the aid of the Cope 3-aza-rearrangement of the enammonium salts (XXXII) has been proposed:[30]

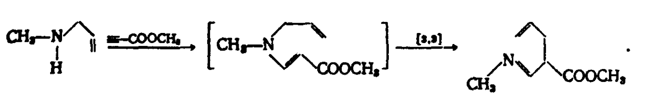


The advantage of this method over that proposed previously[31] is because the allylenamines (XXXI) were obtained by the selective *N*-alkylation of the corresponding allylamines, which made it possible to avoid the difficulties quoted by Opitz et al.[31] associated with the fact that, when vinylamines were used as the initial compounds for the synthesis of structures of type (XXXII), the formation of a mixture of isomers was observed as a result of the simultaneous occurrence of the *C*- and *N*-allylation reactions.

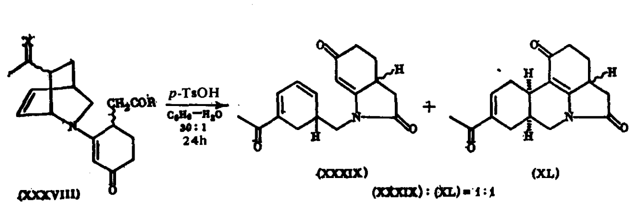
The Cope 3-aza-rearrangement has been used successfully to synthesise the pyridines (XXXIV) from the propargylvinylamines (XXXIII):[32]



The addition of the allylamine (XXXV) to methyl propionate with the subsequent Cope 3-aza-rearrangement of the intermediate (XXXVI) leads to the imine (XXXVII):[33]

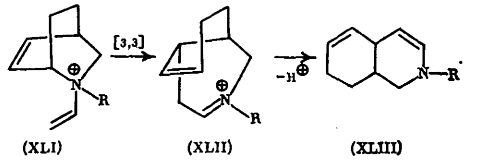


The acid-catalysed reaction of *N*-(β-cyclohexenoyl)isoquinuclidines (XXXVIII), leading to the tetracyclic skeleton of the type of lycorane (XL), has been described in a recently published study[34] in which the investigation[35-39] of the Cope aza-rearrangement initiated previously was continued.



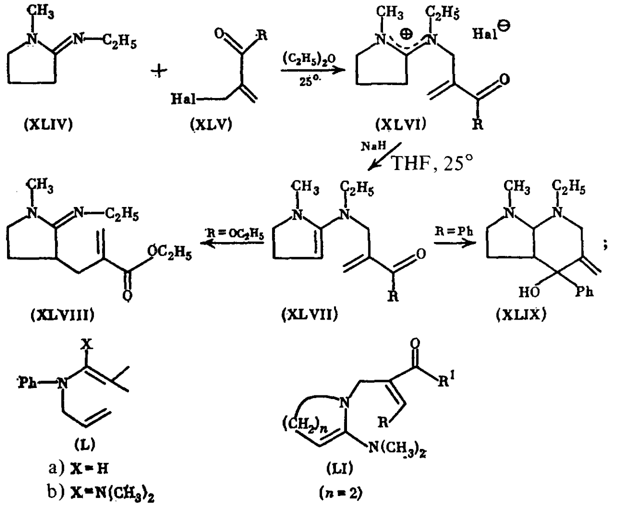
The lactam (XXXIX) is a precursor of the lactam (XL), since only compound (XL) is formed in 40% yield when the reaction is carried out over a period of 48 h.

It is assumed that the hexahydroisoquinoline ring (XLIII) is formed via the elimination of a proton from the intermediate (XLII), which arises from vinylisoquinuclidine (XLI) as a result of the Cope 3-aza-rearrangement:[35]



In certain cases the Cope aza-rearrangement may be accompanied by side reactions (see also Section III). Thus the rearrangement of the amidinium salt (XLVI) via the base (XLVII) leads both to the [3, 3]sigmatropic rearrangement product (XLVIII) and to the product (XLIX) of the intramolecular aldol addition[38] (Scheme 3).

Scheme 3



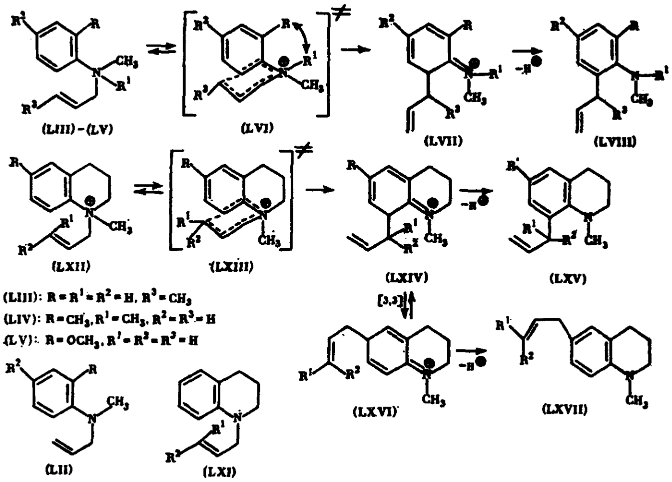
Systems of type (XLVII) merit attention from the standpoint of the elucidation of the influence of electronic factors on the Cope 3-aza-rearrangement, because they contain both electron-donating ($\rangle$N−CH$_3$) and electron-accepting ($-C\begin{smallmatrix}\nearrow R\\ \searrow O\end{smallmatrix}$) substituents. The dialkylamino-group is known to accelerate the Cope oxa-rearrangement.[2] On the other hand, the rearrangement of the amine (La) take place at 170 °C,[26] while that of the diamine (Lb) occurs at 280 °C.[39]

It might have been expected that the simultaneous presence of electron-donating and electron-accepting substituents in a system of type (L) would facilitate the Cope aza-rearrangement. However, it has been found that the rearrangement of the diene (LI), formed from the corresponding amidinium salt on treatment with sodium hydride, takes place even at room temperature and is 10^6–10^8 times faster than the rearrangement of the amine (Lb).[38]

2. Aromatic Cope 3-Aza-rearrangement

The influence of electronic and steric factors on the course of the aromatic Cope 3-aza-rearrangement of *N*-allylanilines [the base (LII) and the salts (LIII)–(LV)][40-42] and the corresponding tetrahydroquinolines (LXI) and (LXII)[42,43] has been investigated in a series of studies by Japanese workers[40–43] (Scheme 4):

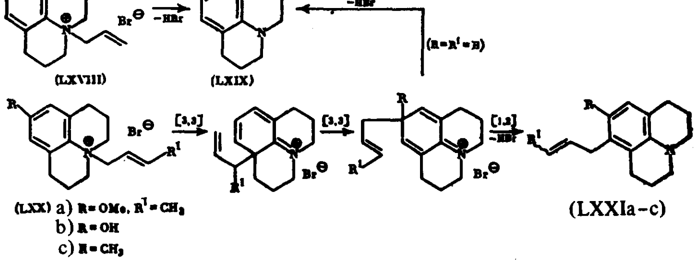
Scheme 4



The concerted reaction mechanism was confirmed in relation to the rearrangement of the *N*-crotyl salt (LIII) (2 : 1 glycerol–water mixture, 140 °C, 4 h). The reaction proceeds via the transition state (LVI) and the aniline (LVIII) with an inverted allyl group is formed. The rearrangement of the quinolines (LXII) takes place via the transition state (LXIII) in the chair conformation, leading to the intermediate (LXIV), from which the quinolines (LXV) and (LXVII) are formed. The intermediate (LXIV) may undergo the usual Cope rearrangement (LXIV) → (LXVI) → (LXVII), which leads to the formation of 6-substituted quinolines (LXVII) with a high stereoisomeric purity. In contrast to anilines with R=H and the quinolines (LXI) and (LXII), the *ortho*-substituted allylanilines (LIV), (LV) afford mainly deallylation and not rearrangement products, which can be accounted for by the steric interaction between the groups R and R^1 in the transition state (LVI).[42] The decrease in the yield of 8-allylquinolines (LXV) on passing from the unsubstituted to the mono- and di-methylallyl groups is associated with increase in the steric interaction of the alkyl groups with the proton in the 8-position in the quinoline ring in the transition state (LXIII).

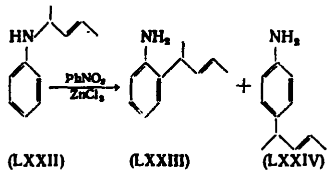
An interesting result has been obtained in the study of the Cope 3-aza-rearrangement of bromo-derivatives of the 4-allyljulolidines (LXVIII) and their 9-substituted analogues (LXXa to c)[41] (Scheme 5). The products (LXXIa-c), involving the rearrangement to the *meta*-position, were discovered first (the analogous Claisen *meta*-rearrangement is known for the reaction of allyl 2,4,6-trimethylphenyl ether in the presence of BCl$_3$ [44]):

Scheme 5



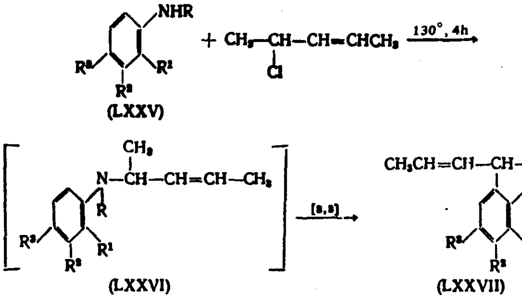
A mechanism involving two consecutive [3, 3]sigmatropic shifts [the transformation (LXVIII) → (LXIX) takes place analogously] and a [1, 2]shift with elimination of a hydrogen bromide molecule has been proposed for the rearrangement (LXX) → (LXXI) (Scheme 5).

The aromatic[45–51] Cope 3-aza-rearrangement of various N-alkenylanilines has been investigated. It has been shown that the rearrangement of *N*-(1-methyl-2-butenyl) aniline (LXXII) is catalysed by the hydrochlorides of aromatic amines and Lewis acids and that the best yield of the corresponding *ortho*- and *para*-alkenylanilines is attained in the presence of ZnCl$_2$ [the yield of (LXXIII) + (LXXIV) is 97%]:[45,50]



An analogous reaction has been achieved for octa,2,7-dienylaniline[46] and *N*-(1-methyl-2-butenyl)-2,5-xylidine.[51]

The rearrangement of *N*-alkenylanilines proved to be an effective method for the synthesis of various *C*-substituted anilines:[47,48]

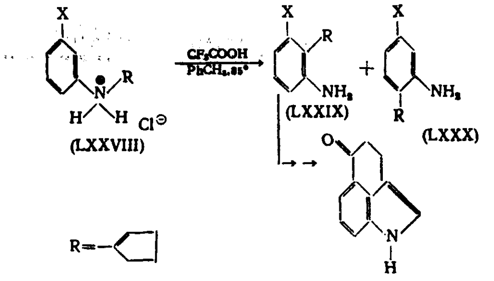


R^1 – R^3 = alkyl, halogen, OCH$_3$,
R = alkyl.

N-Alkenylanilines (LXXVI), formed in the reaction of substituted anilines (LXXV) with 4-chloro-*trans*-pent-2-ene, are immediately converted into the corresponding product (LXXVII) under the reaction conditions.

The kinetics of the acid-catalysed Cope 3-aza-rearrangement of various *N*-allylanilines of type (LXXV) in nitrobenzene have been investigated[49] and it has been shown that in all cases the rearrangement is accompanied by elimination, but that the contribution of the latter is different for different substituents. For equal initial concentrations of aniline and hydrochloric acid, the reaction is described by a first-order equation. The results have been explained from the standpoint of the formation of a contact ion pair from PhNHR.HCl, which can either undergo a rearrangement to 2-allylaniline in the solvent cage or elimination.

The influence of electron-accepting groups on the regioselectivity of the aromatic Cope 3-aza-rearrangement of *meta*-substituted anilinium salts, (LXXVIII) → (LXXIX) → (LXXX), has been studied:[52]

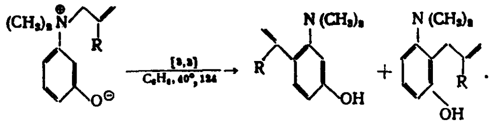


(LXXVIII) (LXXIX) (LXXX) (LXXXI)

	a	b	c	d	e
X	—C≡N	CO_2CH_3	NO_2	F	CF_3
(LXXIX):(LXXX)	2.9:1	(LXXIX) not detected	1:10	1:3.7	1:2

In all cases [with the exception of *m*-cyanoaniline (LXXVIIIa)], the preferential formation of products in the rearrangement to the *p*-position relative to the substituent X was observed. These data have been explained[52] by the steric influence of the group X, because the activation energy for the transition to the isomer (LXXIX) is lower than that for the transition to the isomer (LXXX).[53] The transformation (LXXVIIIa) → (LXXIXa) is of undoubted interest, since it permits the synthesis of the Uhle's ketone (LXXXI), which is a key intermediate on the way to ergot alkaloids.[54]

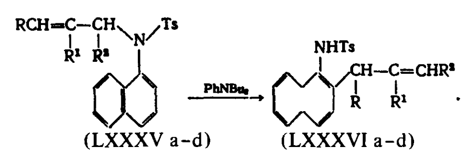
The [3, 3]sigmatropic rearrangement of the betaine (LXXXII) leads to a mixture of the phenols (LXXXIII) and (LXXXIV), the main product being the isomer (LXXXIII) [(LXXXIII):(LXXXIV) = 4:1].[55]



(LXXXII) (LXXXIII) (LXXXIV)

The exceptionally mild reaction conditions are associated with the possibility of the delocalisation of the charge in the course of the rearrangement.[55]

Japanese workers[56] investigated the influence of substituents in the allyl group on the thermal aromatic Cope 3-aza-rearrangement of *N*-allyl-*N*-tosyl-α-naphthylamines (LXXXV) → (LXXXVI):



(LXXXV a-d) (LXXXVI a-d)

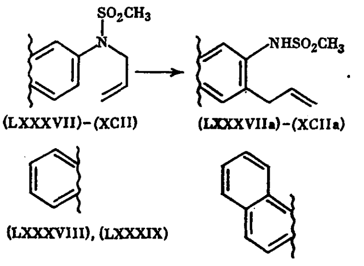
(LXXXV), (LXXXVI)

a) $R{=}R^1{=}H$, $R^2{=}CH_3$
b) $R{=}R^2{=}H$, $R^1{=}CH_3$
c) $R^1{=}R^2{=}H$, $R{=}CH_3$
d) $R^1{=}R^2{=}H$, $R{=}Ph$

The formation of the naphthylamines (LXXXVIa, c, d) from the amines (LXXXVa, c, d) indicates the concerted character of the rearrangement.

In the rearrangement of compounds (LXXXVb), (LXXXVc), and (LXXXVd), the corresponding 4-substituted naphthylamines are formed in addition. The *para*/*ortho* product ratio increases in the series of amines (LXXXVb) < (LXXXVc) < (LXXXVd), which supports the occurrence of consecutive [3, 3]sigmatropic shifts, whose driving force is the steric interaction between the tosylamino-group and the 1-substituted allyl group.

The influence of the aromatic ring on the rate of the thermal Cope 3-aza-rearrangement of *N*-allyl-*N*-methanesulphonylamines [the aniline (LXXXVII), the 1- and 2-naphthylamines (LXXXVIII) and (LXXXIX), and the 2-, 3-, and 9-phenanthrylamines (XC), (XCI), and (XCII)] in *NN*-dibutyl-aniline containing a small amount of triphenylphosphine has been studied:[57]



(LXXXVII)-(XCII) (LXXXVIIa)-(XCIIa)

(LXXXVIII), (LXXXIX)

(XC)-(XCII)

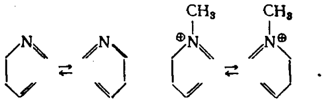
In all cases the rearrangement (LXXXVII) → (XCII) → (LXXXVIIa) → (XCIIa) obeys a first-order kinetic equation and has negative activation entropies, which suggested a concerted process mechanism.[57]

The highest rate of rearrangement has been observed for *N*-allyl-*N*-methanesulphonyl-1-naphthylamine (LXXXVIII) and *N*-allyl-*N*-methanesulphonyl-9-phenanthrylamine (XCII). The data (ln *k*) obtained are satisfactorily correlated ($r = 0.991$; $s = 0.290$) with the corresponding delocalisation energies.

An analogous correlation of the logarithms of the rate constants with the localisation energies has been observed also for the Claisen rearrangement of the corresponding o-allyl ethers of phenol, naphthol, and phenanthrol ($r = 0.999$; $s = 0.110$).[57]

III. THE COPE 2-AZA-REARRANGEMENT

The Cope 2-aza-rearrangement of 3-butenylimines (XCIII) is degenerate:

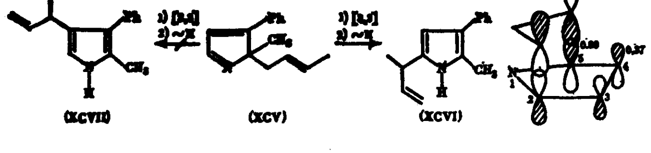


(XCIII) (XCIII) (XCIV) (XCIV)

The equilibrium position in substituted systems of type (XCIII) can be established on the basis of "secondary" structural factors such as, for example, steric interactions or the conjugation effect in the reactants and products.[7] A number of instances of rearrangements of systems (XCIII) and (XCIV) have been quoted in a review.[7] It has been established that, as a rule, iminium salts of type (XCIV) rearrange under much milder conditions than the isoelectronic type (I) Cope systems and the rearrangement is faster than the reaction of the uncharged imine (XCIII).[7]

One of the latest studies devoted to the comparative investigations of the Cope rearrangement and its 2-aza-analogue has been carried out by French investigators.[58] The thermolysis of the model 2*H*-pyrrole (XCV), which has no substituents in the 4- and 5- positions (170 °C, 3.5 h), led to the isolation in 90% yield of one product (XCVI), whose formation has been explained by the Cope 2-aza-rearrangement with subsequent migration of hydrogen:

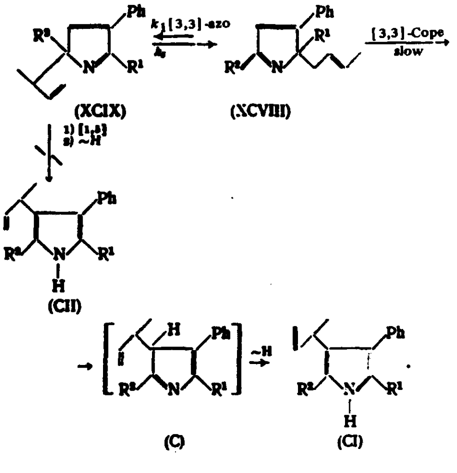
Scheme 6



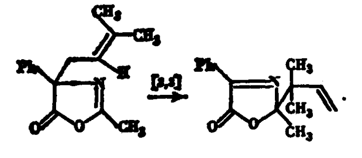
The following conclusions have been reached concerning the possibility of the migration of the *trans*-crotyl group.[58] If the 2*H*-pyrrole is unsubstituted in the 3- and 4-positions, then the [1, 5]shift to the 3-position takes place; when the 4-position is the only one remaining free, the Cope rearrangement [migration to C(4)] is observed; finally, when the 4- and 5-positions are free, only the Cope 2-aza-rearrangement [migration to C(5)] takes place. The absence of the Cope rearrangement (XCV) → (XCVII) has been explained by the difference in the interaction of the frontier orbitals of pyrrole and the allyl group in the two transition states leading respectively to the Cope reaction and the Cope 2-aza-reaction. The difference between the amplitudes of the atomic orbitals of the carbon atoms in the 4- and 5-positions demonstrates the possibility of the migration to the C(4) atom[58] (Scheme 6). The data obtained in the above study made it possible to account for earlier experimental observations.[59,60]

The finding that the thermolysis of the pyrrole (XCVIII) does not lead to the product (XCIX) of the Cope aza-rearrangement[60] can be logically explained by the following factors: firstly, the rate constant k_2 for the reversible isomerisation (XCVIII) ⇄ (XCIX) is higher than k_1; secondly, the slower Cope reaction converts the pyrole (XCVIII) into the 3*H*-pyrrole (C), which isomerises irreversibly to the pyrrole (CI); thirdly the 1,5-migration with formation of the pyrrole (CII) is not observed when the 3-position is substituted[58] (Scheme 7):

Scheme 7



The Cope 2-aza-rearrangement has been observed in the series of oxazoles.[61] Thus the thermolysis (162 °C, benzene) of allyl-substituted Δ^2-oxazolinones leads to the Δ^3-oxazolinone system:

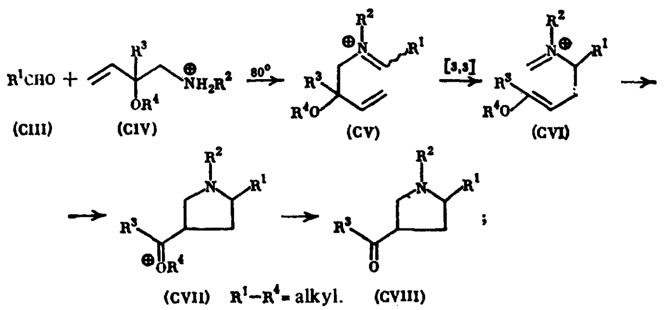


The formation of 2-(1,1-dimethyl-2-propenyl)-Δ^3-oxazolinone shows that the reaction proceeds via the [3, 3]sigmatropic and not the [1, 3]sigmatropic shift.[61]

In recent years the Cope 2-aza-rearrangement has been widely used by several groups of investigators for the synthesis of various heterocyclic systems.

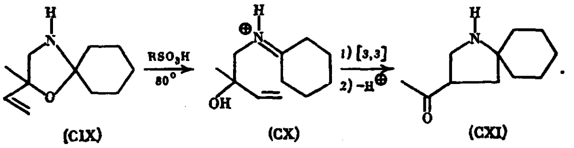
A series of studies[62-71] have been devoted to the "directed" Cope 2-aza-rearrangement of charged systems of type (XCIV). The condensation of the aldehyde (CIII) with salts of secondary amines (CIV) leads to the iminium salts (CV), which undergo the [3, 3]sigmatropic rearrangement to the intermediates (CVI), which are further transformed via the oxonium cation (CVII) into the acylpyrrolidines (CVIII) in 80 to 95% yield[62] (Scheme 8):

Scheme 8

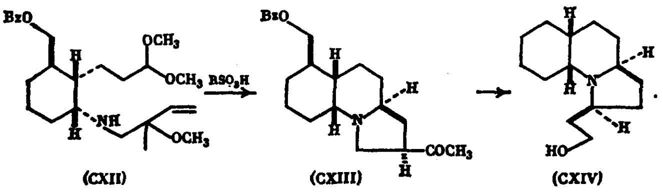


The reaction described constitutes a new method of synthesis of the pyrrolidine ring. The cationic Cope aza-rearrangement and the Mannich reaction have been used consecutively to synthesise poly-substituted pyrrolidines of type (CVIII) (isoprene) derivatives were used as the initial compounds).[69]

It has been shown[63] that the imminium ion (CX) [an analogue of the ion (CV)] can be generated from the oxazolidine precursor (CIX), which permitted the synthesis of substituted 1-aza-spiro-[4, 5]decanes (CXI):

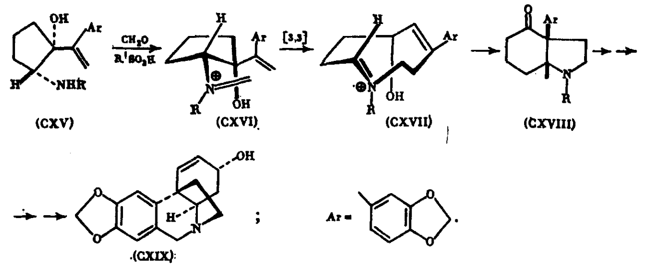


A reaction in which the iminium ion is formed intramolecularly has been used for the single-stage synthesis of the indolizine (CXIII) [(CXII) → (CXIII)],[70] which is a key compound on the way to the alkaloid DL-perhydrogenphyrotoxin (CXIV):



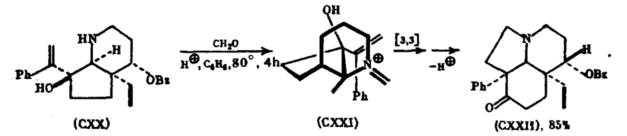
A novel method of synthesis of the pyrrolidine ring, involving the consecutive occurrence of two processes, namely ring expansion and contraction, has been demonstrated in the synthesis of *cis* 3a-aryl-octahydroindolones [Scheme 8, (CXV) → (CXVIII), R = $CHPh_2$].[64,66] This reaction makes it possible to achieve a new stereoselective synthesis of the alkaloid crinin (CXIX).

Scheme 8a



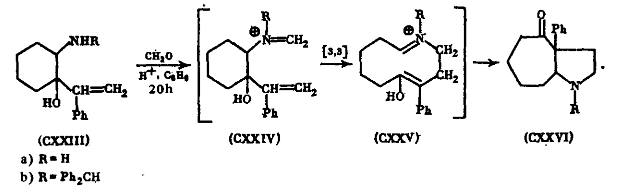
The formation of the *cis*-product (CXVIII) follows from the *trans*-orientation of the amino- and vinyl groups in the amine (CXV). As a result of such *trans*-disposition, the iminium ion undergoes the Cope 2-aza-rearrangement via the only possible transition state in the chair conformation, affording *trans*, *trans*-azacyclonona-1,6-diene (CXVII). The latter is converted stereospecifically into the *cis*-intermediate (CXVIII) after the intramolecular Mannich ring closure.

The above method of ring expansion with the subsequent formation of the pyrrolidine ring has been used successfully for the synthesis of the complex 9a-arylhydrolilodine system [(CXX) → (CXXII)], which is the basis of the *Aspidosperma* alkaloids:[65]



The synthetic possibilities of the cationic Cope 2-aza-rearrangement have also been demonstrated in relation to the stereospecific synthesis of *cis*- and *trans*-3a-aryl-4-oxodecahydrocyclohepta[*b*]pyrroles (CXXVI):[67,68,71]

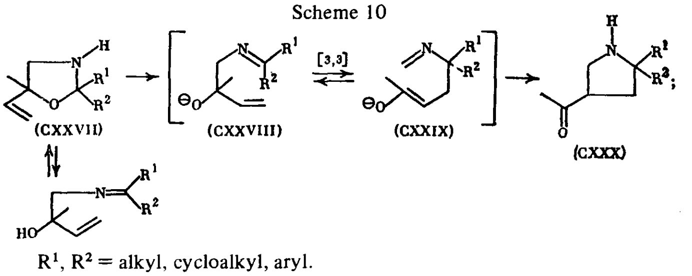
Scheme 9



In the case of the cyclohexanols (CXXIIIa, b), with the *trans*-disposition of the vinyl and amino-groups, the rearrangement leads to the *cis*-pyrrolidine (CXXVI) via the iminium cation (CXXIV) and the intermediate *trans*, *trans*-azacyclodeca-1,7-diene (CXXV) (cf. with Scheme 8a).

Instances of the Cope 2-aza-rearrangement enumerated above (see, for example, Overman and co-workers[62,63]) are either thermal or acid-catalysed processes. However, it has been shown[65] that the above rearrangement can be achieved under exceptionally mild conditions in the presence of a base (Scheme 10):

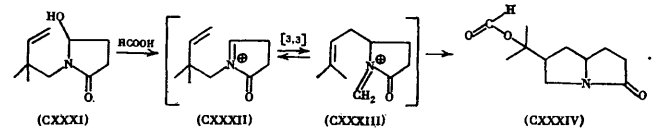
Scheme 10



R^1, R^2 = alkyl, cycloalkyl, aryl.

On heating in THF (at 25 °C) for 24 h in the presence of 1.5 equivalents of KH and 0.1 of an equivalent of 18-crown-6 ether, 5-vinyl-oxazolidines (CXXVII) give rise to the pyrrolidines (CXXX) in 50–90% yield. Potassium hydride converts the oxazolidine (CXXVII) into the intermediate (CXXVIII), which undergoes the [3,3]sigmatropic rearrangement to the enolate anion (CXXIX), which effects ring closure to 3-acetylpyrrolidine (CXXX) via the intramolecular endocyclic attack on the imino-group. The transformation (CXXVII) → (CXXX) constitutes the first example of the base catalysis of the Cope hydroxy-2-aza-rearrangement (the acceleration of the usual Cope hydroxy-rearrangement by bases is well-known[73–76]).

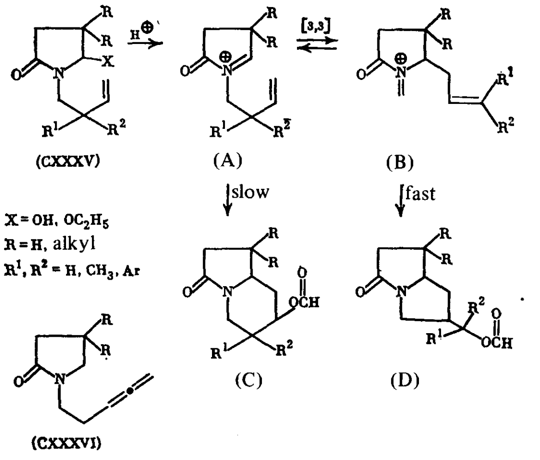
The Cope 2-aza-rearrangement of *N*-acyliminium salts has been used in a number of studies to synthesise heterocyclic systems.[77–81] A rearrangement of this kind was described for the first time in a study[77] where it was shown that treatment of the carbinolamide (CXXXI) with formic acid leads to the pyrrolizidinone (CXXXIV):



A key stage is the Cope 2-aza-rearrangement of the *N*-acyliminium ion (CXXXII) with the subsequent cyclisation of the intermediate (CXXXIII) to the formate (CXXXIV). Later this method was used to synthesise a series of pyrrolizidine bases.[78]

The mechanism of the Cope 2-aza-rearrangement of *N*-acyliminium salts has been investigated[79–81] and it has been established that the pyrrolidinones (CXXXV)–(CXXXVI) can react via two pathways in an acid medium.[79–81] One of them leads to the pyrrolizidine system (P)[80,81] and the other leads to the indolizidines (C) (Scheme 11).

Scheme 11



Both processes proceed via a stage involving the formation of the "secondary" iminium ion (A), which either undergoes the reversible Cope 2-aza-rearrangement to the "primary" iminium ion (B) and then rapidly cyclises (the relevant kinetic data have been published[81]) to the pyrrolizidine (D) or is immediately converted into the indolizidine (C) in a slow stage. The lactams (CXXXVI) containing an allene residue react analogously. The pathway followed in the reactions of the lactams (CXXXV) and (CXXXVI) and the ratio of the products (C) and (D) depend on the nature of the groups R, R^1, and R^2 in the pyrrole ring and in the allyl component of the molecule.[79-81]

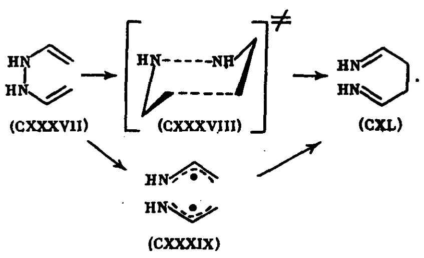
IV. THE COPE 3,4-DIAZA-REARRANGEMENT

As stated in the introduction, the Cope 3,4-diaza-rearrangement of the enehydrazines (VII) and (X) is in essence a stage in the formation of the C–C bond in the Fischer indole synthesis and in the Piloty pyrrole synthesis.

The idea that these reactions be considered from the standpoint of [3, 3]sigmatropic rearrangements was first put forward in two reviews.[11,13] A number of studies devoted to the elucidation of the mechanism of the thermal and acid-catalysed Cope 3,4-diaza-rearrangements have been discussed in a monograph.[7] New results demonstrating the validity of the approach to the mechanism of the rearrangement of enehydrazines from the standpoint of the theory of concerted processes have been obtained in recent years.

The rearrangement of the model divinylhydrazine (CXXXVII) has been investigated[82] by the MINDO/3 method (Scheme 12).

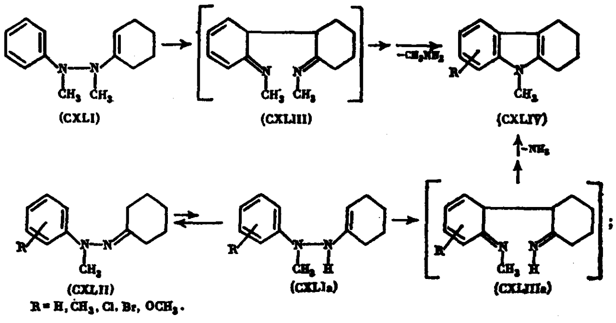
Scheme 12



The MINDO/3 calculation showed that the transition state (CXXXVIII) in the [3, 3]sigmatropic migration (CXXXVII) → (CXL) has the chair structure (C_2 symmetry), which indicated an analogy with the rearrangement of hexa-1,5-diene.[8] The multistage mechanism involving the formation of the radical pair (CXXXIX) is energetically less favourable (by 8.2 kcal mol^{-1}) than the concerted mechanism, but such a small difference between the energies of the two migration mechanisms does not allow the complete exclusion of homolysis from the general scheme of the rearrangement[82] (the concerted mechanism of the Cope rearrangement involving hexa-1,5-diene is more favourable to the extent of 33.4 kcal mol^{-1} than the multi-stage mechanism[83]).

Experimental confirmation of the concerted mechanism in the stage involving the formation of the carbon–carbon bond in the Fischer reaction, (CXLI) → (CXLIII) and (CXLIa) to (CXLIIIa), has been obtained on the basis of kinetic data for the rearrangement of *NN'*-dimethyl-*N*-phenyl-*N'*-(1-cyclohexenyl)hydrazine (CXLI) and substituted cyclohexanone *N*-methyl-phenylhydrazones (CXLII) to the tetrahydrocarbazoles (CXLIV)[82,84] (Scheme 13).

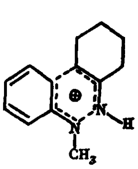
Scheme 13



It has been established that both the thermal and acid-catalysed rearrangements of the enehydrazine (CXLI) are faster than the corresponding reactions of the hydrazones (CXLII), which indicates a significant contribution by the stage (CXLII) → (CXLIa) to the overall rate of the process.[82] Substituents of different types and solvent polarity have little influence on the rate of conversion of the hydrazones (CXLII) into indoles, which proceeds in accordance with a first-order equation and in addition this reaction has fairly high negative activation entropies in all cases.[82,84]

The acidity of the medium has an appreciable influence on the rate of the transformations (CXLI) → (CXLIV) and (CXLII) → (CXLIV). Thus the factor by which the sulphuric acid-catalysed (two moles of acid per mole of reactant) rearrangement of the enehydrazine (CXLI) is accelerated compared with the thermal rearrangement at 60 °C is ~400,[82] which agrees with other data.[85,86]

This finding supports the charge-induced pericyclic reaction.[20] This reaction takes place so rapidly because the positive charge in the six-membered transition state (CXLV) is delocalised between the six atoms of the reacting system. An analogous acceleration has been observed in the aromatic Cope 3-aza-rearrangement (Section II).

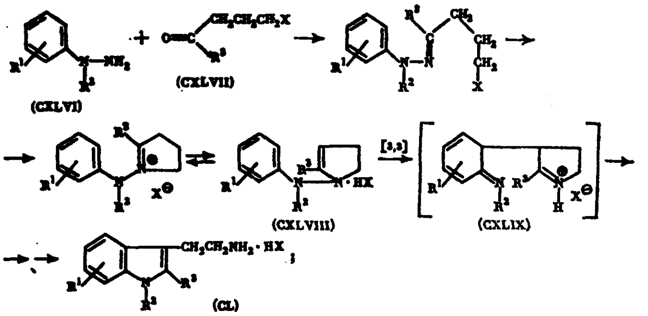


(CXLV)

The main stage in the synthesis of the tryptamines (CL) and related structures from γ-halogenocarbonyl compounds (CXLVII) (or their δ-analogues) and the arylhydrazines (CXLVI), namely the formation of the C–C bond via the reaction (CXLVIII) → (CXLIX), is also a type of the Cope 3,4-diaza-rearrangement and proceeds via the mechanism of the

[3,3]sigmatropic rearrangement (Scheme 14) (see the relevant review[87] and the literature quoted therein).

Scheme 14



$R^1 - R^3$ = alkyl, aryl, arylalkyl; X = halogen.

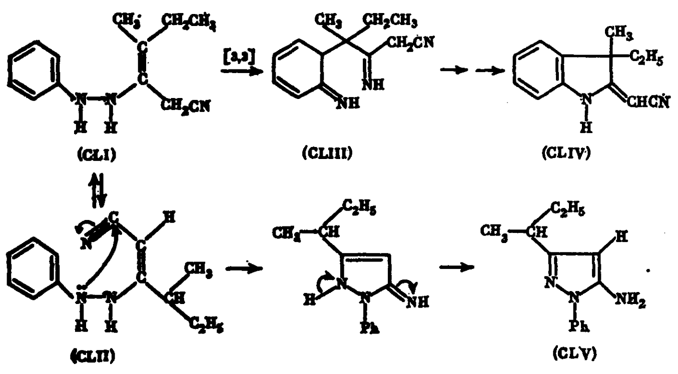
This reaction is a special case of the Fischer indole synthesis without the evolution of ammonia.

Numerous studies of various aspects of the mechanism of the Fischer reaction have been published in recent years. Thus the possibility of the formation of intermediates and their structures has been investigated by ^{13}C NMR,[88] ^{15}N NMR,[89] and mass spectrometry.[90] The influence of the electronic and steric factors on the direction of the indole formation reaction, its mechanism, and the ratio of the isomeric products has been studied.[91–100] The results of the comparative investigation of the Fischer indole synthesis and of the "anomalous" [3,5]- and [5,5]-sigmatropic rearrangement of various o-substituted arylhydrazones and also the migration of the substituents in these systems have been discussed in detail in a review[103] and recent communications.[102,103]

The authors of the above studies[91–103] adhere to the concept of the concerted character of the carbon–carbon bond formation stage in the Fischer reaction.

An interesting example of the Cope 3,4-diaza-rearrangement, namely (CLI) → (CLIII) has been observed for the adduct (CLI) formed in the reaction of phenylhydrazine with an allene nitrile[104] (Scheme 15):

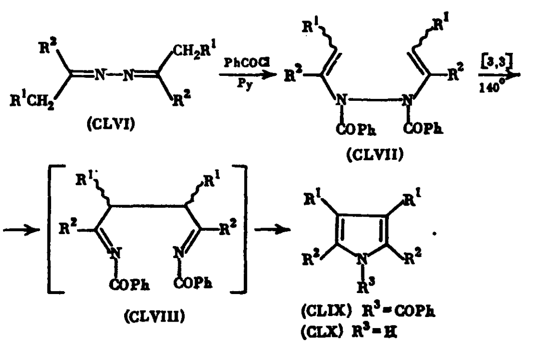
Scheme 15



Since the enehydrazine (CLII) (isolated in a pure state) does not undergo the [3,3]sigmatropic rearrangement and gives rise to the pyrazole (CLV), the formation of the indoline (CLIV) from this enehydrazine can be explained by the prototropic isomerisation (CLII) → (CLI) with the subsequent Cope 3,4-diaza-rearrangement.[104]

The latest advances in the chemistry of the enehydrazines of type (VIII), including their ability to undergo the Cope 3,4-diaza-rearrangement with formation of pyrrole systems, have been analysed in detail in a review.[105]

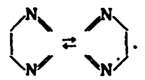
We shall mention only the study[106] in which a general method has been proposed for the synthesis of the pyrroles (CLIX) and (CLX) from the azines of the enolysable aldehydes and ketones (CLVI) via the concerted thermal rearrangement (CLVII) → (CLVIII) of the benzoyl derivatives (CLVII):



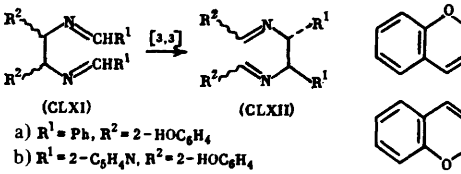
The dienehydrazines (CLVII), which are fairly stable compounds (characterised by ^{1}H NMR), have been used in the synthesis of the pyrroles (CLIX) without isolation. The hydrazinolysis of the latter made it possible to obtain readily the pyrroles (CLX).

V. THE COPE 2,5-, 2,3-, AND 1,3-DIAZA-REARRANGEMENTS

The Cope 2,5-diaza-rearrangement is in the general case a reversible process and in the absence of substituents is a degenerate process:



However, the directed Cope 2,5-diaza-rearrangement (CLXI) → (CLXII)[107] has been achieved for the double Schiff base (CLXI) containing the 2-hydroxyphenyl group (see also Heimgartner et al.[7]). The subsequent hydrolysis of the diimine (CLXII) leads to a carbonyl compound and *meso*-1,2-diaryl-1,2-ethylenediamine:

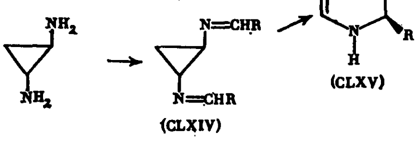


a) R^1 = Ph, R^2 = 2-HOC_6H_4
b) R^1 = 2-C_5H_4N, R^2 = 2-HOC_6H_4

In the given instance the relative stability of the diimines (CLXIIa) and (CLXIIb) is due to the presence of the intramolecular hydrogen bond between the imine nitrogen atom and the phenolic hydroxyl.

The possibility of the thermal Cope 2,5-diaza-rearrangement was first demonstrated in 1965 for *trans*-1,2-bis(benzylideneamino)cyclopropane (CLXIV, R = Ph); the reaction yielded 2,3-diphenyl-2,3-dihydro-1*H*,1,4-diazepine (CLXV)[108] (Scheme 16). However, the stereochemistry of the process remained unelucidated.

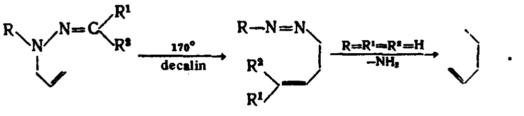
Scheme 16



The thermal rearrangement of the *cis*- and *trans*-bisimines (CLXIII) and (CLXIV) (R = t-butyl, phenyl, *p*-tolyl, or mesityl), formed from the corresponding diaminocyclopropanes, has been investigated.[109] It was found that in all cases the only reaction product is a *cis*-substituted dihydrodiazepine (CLXV). This result demonstrates that the Cope 2,5-diaza-rearrangement involves one structure with the same configuration at both C=N bonds [for the imine (CLXIII) this is the *EE*-configuration]. A strong influence of the t-butyl groups on the rearrangement of the bis-imines (CLXIII) and (CLXIV) has been observed. Thus the *cis*-imine (CLXIII, R = t-Bu) is only slowly converted into the diazepine (CLXV) at 100 °C (93 h, yield 49%), while the reaction of *cis*-diaminocyclopropane with benzaldehyde at 0 °C leads to a 90% yield of the diazepine (CLXV, R = Ph). This effect can be explained by the fact that, in the formation of the C(2)–C(3) bond in 2,3-dihydro-1,4-diazepine, the substituents must have an eclipsed disposition, and in the case of two t-butyl groups this destabilises the molecule to the extent of 63 kJ mol^{-1}.[109]

We may note that the Cope 2,5-diaza-rearrangement, illustrated in Scheme 16, constitutes one of the important preparative methods whereby it is possible to achieve ring expansion by four units at once with formation of a heterocyclic system (the Claisen rearrangement and the Cope hydroxy-rearrangement have also been studied for this purpose, but these processes involve the formation of carbocyclic compounds[110]).

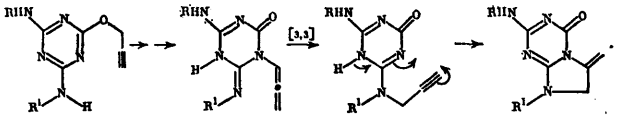
The Cope 2,3-diaza-rearrangement of *N*-alkyl-*N*-allylhydrazones (CLXVI) has been proposed for the preparative synthesis of the γδ-unsaturated azo-compounds (CLXVIII)[111] [the thermolysis of the hydrazone (CLXVII) led to the alkene (CLXIX)[112]]:



(CLXVI), (CLXVII) (CLXVIII) (CLXIX)
(CLXVII): R=R¹=R²=H

The Cope 2,3-diaza-rearrangement has also been observed in the vacuum pyrolysis of *N*-allyloxadiazolinones.[113] For charged systems, this reaction has not been described in the literature.

One of the stages in the thermal[114] and catalytic [$(CF_3COO)_2$][115] transformations of the propargyl ethers of hydroxytriazine (CLXX) into imidazo[1,2-*a*]-1,3,5-triazines (CLXXIII) can be regarded as the Cope 1,3-diaza-rearrangement (CLXXI) → (CLXXII):



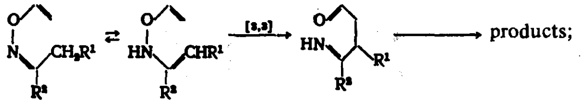
(CLXX) (CLXXI) (CLXXII) (CLXXIII)

VI. THE COPE POLYHETERO-REARRANGEMENTS

The rearrangements of systems containing oxygen and sulphur atoms in addition to nitrogen atoms, i.e. the Cope oxaza- and thiaza-rearrangements are considered in this section.

1. The Cope Oxaza-rearrangement

The [3,3]sigmatropic rearrangement in which the nitrogen–oxygen bond dissociates (thermal rearrangement or rearrangement in the presence of acids) was described in 1971 in relation to *O*-aryl- and *O*-vinyl-oximes:[116]

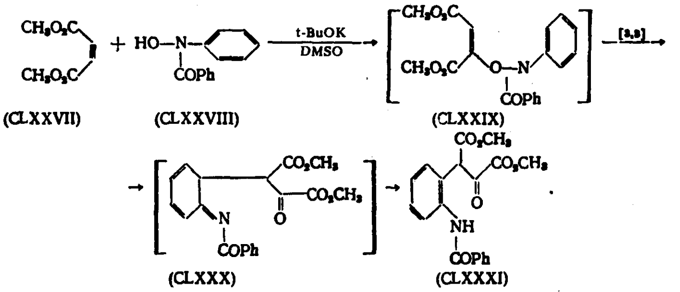


(CLXXIV) (CLXXV) (CLXXVI)
R^1, R^2 = H, alkyl, aryl.

Presumably the fairly severe reaction conditions are necessary only for the isomerisation of the oxime (CLXXIV) → (CLXXV), while the stage involving the rearrangement proper (CLXXV) → (CLXXVI) should occur spontaneously under mild conditions by virtue of the relatively weak and highly polar N–C bond.

Indeed it has been found that if the Cope hetero-system of type (CLXXIX) is produced directly by the addition of *N*-phenylbenzohydroxamic acid (CLXXVIII) to dimethyl acetylenedicarboxylate (CLXXVII), then the rearrangement (CLXXIX) → (CLXXX) takes place readily (20 °C, 1 h) and leads to the ester (CLXXXI) in a high yield[117] (Scheme 17):

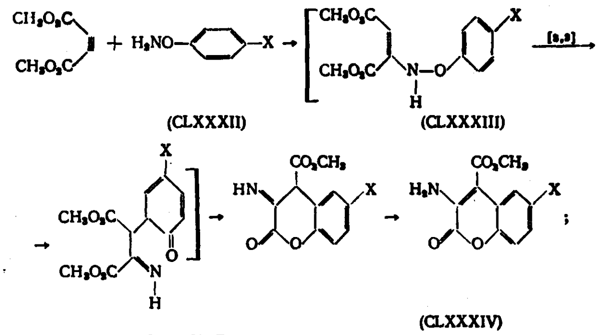
Scheme 17



(CLXXVII) (CLXXVIII) (CLXXIX) (CLXXX) (CLXXXI)

The addition of *p*-substituted *O*-arylhydroxylamines (CLXXXII) to)CLXXVII) (ethanol, 20 °C, 2 h) takes place in the absence of alkaline catalysts and the adduct (CLXXXIII) formed is converted via a stage involving the [3,3]sigmatropic shift into 3-aminocoumarins (CLXXXIV)[117] (Scheme 18):

Scheme 18

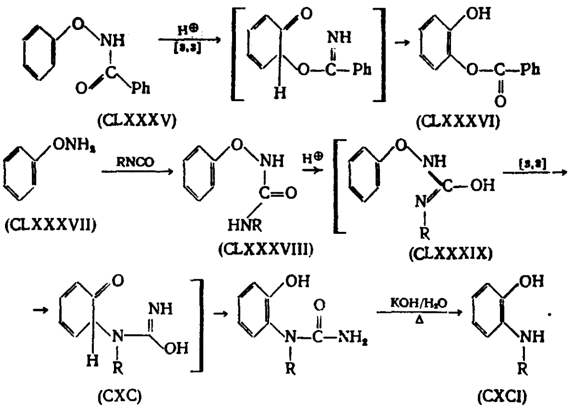


(CLXXXII) (CLXXXIII) (CLXXXIV)
X=H, CH_3, Cl, Br.

The acid-catalysed Cope oxaza-rearrangement is the principal stage in the reactions of derivatives of *O*-arylhydroxylamines described by a group of Japanese investigators[118,119]

(Scheme 19). It is of interest that the hetero-hexa-1,5-diene systems (CLXXXV) and (CLXXXIX) contain three heteroatoms, which increases their reactivity:

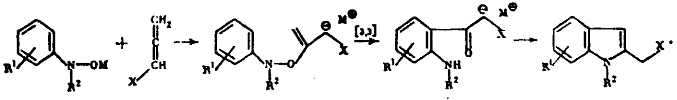
Scheme 19



Thus treatment of *N*-benzoyl-*O*-phenylhydroxylamine (CLXXXV) with a 5:1 mixture of trifluoroacetic and trifluoromethanesulphonic acids for 24 h at 20 °C leads to a high yield of *o*-hydroxyphenyl benzoate (CLXXXVI),[118] while the urea derivative (CLXXXVIII) readily gives rise to 2-alkylaminophenols (CXCI) in dichloromethane at room temperature.[119]

The Cope oxaza-rearrangement has been used in a number of instances for the synthesis of the indole ring.[120–123] 2-Substituted indoles (CXCVI) are readily formed from derivatives of *N*-phenylhydroxylamine (CXCII) and allenes with electron-accepting substituents (CXCIII).[120] The key stage in this synthesis is the formation of *o*-substituted anilines (CXCV) via the [3,3]sigmatropic rearrangement (CXCIV) → (CXCV) (Scheme 20):

Scheme 20



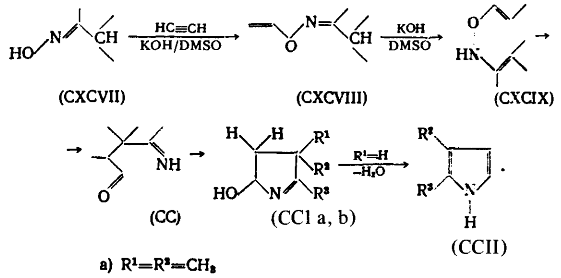
R^1 = H, 4-CH_3, 3-OH, 4-Cl; X = SO_2Ph
R^2 = $COCH_3$, $COCH_2Ph$, C_2H_5; M = Li, Na, K

The anilide (CXCV, R^1 = 4-CH_3, R^2 = $COCH_3$, X = So_2Ph) has been obtained in 90% yield from the corresponding salt of the hydroxamic acid (CXCII) at room temperature in the course of 10 min while in the reaction involving the use of *N*-alkylphenylhydroxylamines (R^1 = H, R^2 = C_2H_5) spontaneous conversion into the indole (CXCVI) was observed.

An additional cause of the extremely great ease of the Cope oxaza-rearrangement (CXCIV) → (CXCV) (apart from the lability of the N–O bond) is the presence in the molecule of compound (CXCIV) of a carbanionic centre, which is known to accelerate the Cope rearrangement[124] and the Cope hydroxy-rearrangement.[125] Derivatives of *N*-phenylhydroxylamine have also been used to synthesise 2,3-unsubstituted indoles,[121] pyrrolo[1,2-*a*]indole,[122,123] and 2-substituted *N*-acylindoles.[126,127] All the reactions indicated proceed via a stage involving the [3,3]sigmatropic shift, analogous to that illustrated in Scheme 20.

The Cope oxaza-rearrangement of derivatives of *N*-arylhydroxylamine has also been used for the regioselective acylamination of the benzene ring[128] and the synthesis of *o*-acyloxyanilides.[129]

Data confirming the concerted variant of the mechanism of the reaction involving the formation of pyrroles from ketoximes and acetylene[132] proposed previously[131] have been published:[130]

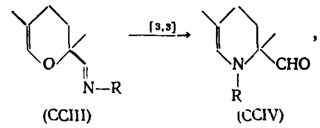


a) $R^1=R^2=CH_3$
b) R^1=H, R^2=iso-C_3H_7, R^3=Ph

The vinyloxyimine (CXCVIII), obtained from the ketoxime (CXCVII) and acetylene in the superbasic catalytic system KOH–dimethyl sulphoxide system, isomerises to the *ON*-divinylhydroxylamine (CXCIX), which undergoes the Cope oxaza-rearrangement to the intermediate (CC), which has been isolated in the form of the dihydropyrrole (CCI). On heating, the latter is readily converted into the pyrrole (CCII).[130]

Apart from the examples of the Cope oxaza-rearrangement, occurring with dissociation of the N–O bond, which has been described above, reactions are known for the hexa-1,5-diene system in which the nitrogen and oxygen atoms are not linked directly to one another.

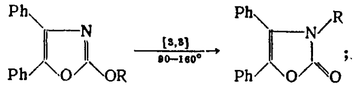
Thus dihydropyranimines (CCIII) have been made to undergo a thermal (200–250 °C) rearrangement to the aldehydes (CCIV) via the mechanism of the Cope oxaza-rearrangement:[133]



where R = s-butyl, benzyl, phenyl, or cyclohexyl.

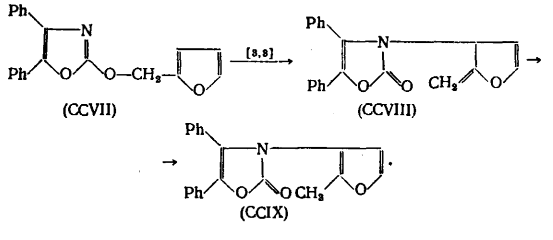
An analogous scheme has been proposed for the rearrangement of *O*-cyclohexynyl carbimidates.[134]

The thermal rearrangement of 2-allyloxyoxazoles (CCV) to 2-oxazolinones (CCVI) has been described:[135,136]



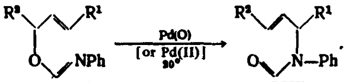
R = allyl, substituted allyl.

The hypothesis that the reaction (CCV) → (CCVI) proceeds via the stage of the [3,3]sigmatropic rearrangement has been confirmed by the isolation of the intermediate (CCVIII) on heating the oxazole (CCVII) in a benzene–pyridine mixture:[136]



On heating or in the presence of acids, the adduct (CCVIII) is converted into the oxazolinone (CCIX).

The use of the complex palladium catalysts $Pd(PPh_3)_4$ and $Pd(PhCN)_2Cl_2$ makes it possible to carry out the Cope oxaza-rearrangement under mild conditions.[137] *O*-allyl *N*-phenylformimidates (CCX) readily rearrange at room temperature to the corresponding *N*-allyl-*N*-phenylformamides (CCXI):



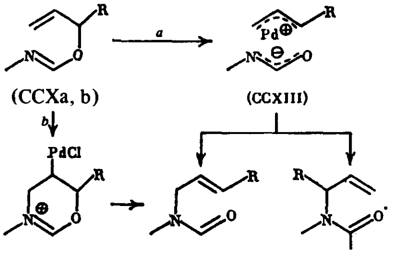
(CCX) (CCXI)

a) R^1=CH_3, R^2=H
b) R^1=H, R^2=CH_3

It has been shown that the regioselectivity of the rearrangement (CCX) → (CCXI) depends on the nature of the palladium complex. Thus catalysis by the palladium(II) complex of the rearrangement of the imidates (CCXa) and (CCXb) leads solely to the corresponding formamides (CCXIa) or (CCXIb), while a zerovalent palladium complex affords in both cases a 2:1 mixture of the products (CCXIa) and (CCXIb) (it is noteworthy that the stereochemistry of the process has not been rigorously established.

These results can be explained by two possible mechanisms of the interaction of the palladium complex with the hexadiene system (CCX)[137] (Scheme 21):

Scheme 21

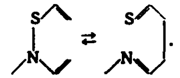


(CCXa, b) (CCXIII) (CCXII) (A) (B)

The zerovalent palladium complex catalyses the rearrangement proceeding via the formation of the allyl π-complex (CCXIII) by its oxidative addition to the C–O bond of the formimidate (pathway *a*). There is then a possibility of the formation of two isomers (A) and (B). On the other hand, the palladium(II) complex tends to form the six-membered intermediate (CCXII) (pathway *b*), which leads to only one product (A) [an analogous mechanism has been proposed for the Cope rearrangement catalysed by palladium(II)[138] and mercury(II)[139] complexes].

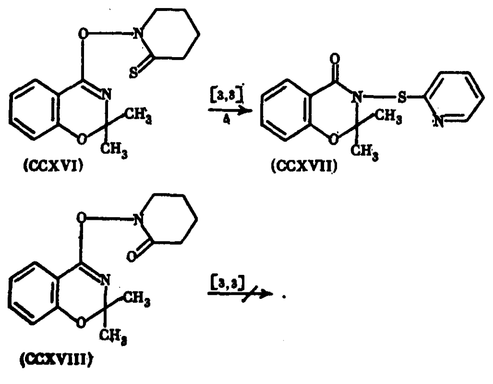
2. The Cope Thiaza-rearrangement

The Cope thiaza-rearrangement has a number of features which distinguish it from the oxaza-analogue. Firstly, systems of type (CCXIV), for which the transformation (CCXIV)→(CCXV) would be possible (see, for example, Padwa and Cohen[136]), are unknown:



(CCXIV) (CCXV)

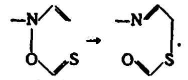
On the other hand, the formation of the S–N bond [i.e. the transition (CCXV) → (CCXIV), which has not been observed for the *ON*-system] via the thermal [3,3]sigmatropic rearrangement of the benzoxazine (CCXVI) to the benzoxazinone (CCXVII) has been described:[140]



(CCXVI) (CCXVII) (CCXVIII)

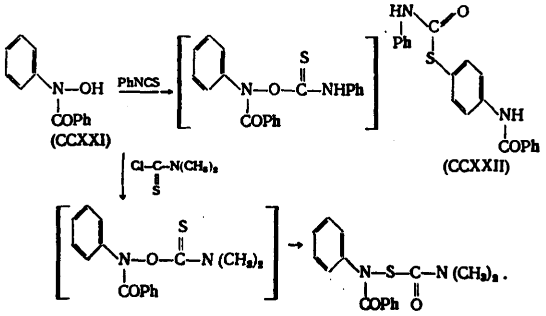
The possibility of the reaction (CCXVI) → (CCXVII) evidently arises not only from the presence of four heteroatoms and the labile N–O bond in the reacting system (CCXVI) but also from the adequate stability of the N–S bond formed, because the benzoxazine (CCXVIII) is not involved in a similar rearrangement.[140]

At the same time the attempts to achieve a concerted reaction of the type (CCXIX) → (CCXX) were unsuccessful:



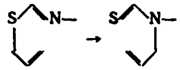
(CCXIX) (CCXX)

Thus the interaction of *N*-benzoyl-*N*-phenylhydroxylamine (CCXXI) with phenyl isothiocyanate[141] and dimethylthiocarbamoyl chloride[142] led to the formation of the products of the *n*-rearrangement [compound (CCXVII)] and 1,3-migration [compound (CCXXIII)] respectively, which virtually rules out a concerted mechanism:



(CCXXI) (CCXXII) (CCXXIII)

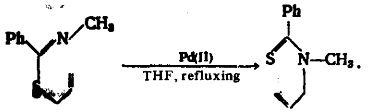
The rearrangement of *S* allyl thiomidates (CCXXIV) → (CCXXV) has been investigated in a number of studies:[143–147]



(CCXXIV) (CCXXV)

It has been shown[143] that the rearrangement of allylthiocaprolactam proceeds via a zwitter-ionic intermediate and not via a concerted mechanism.

Palladium(II) salts [$PdCl_2$ or $PdCl_2(PhCN)_2$ [144]] proved to be effective catalysts of the Cope thiaza-rearrangement of *S*-allyl thioimidates:

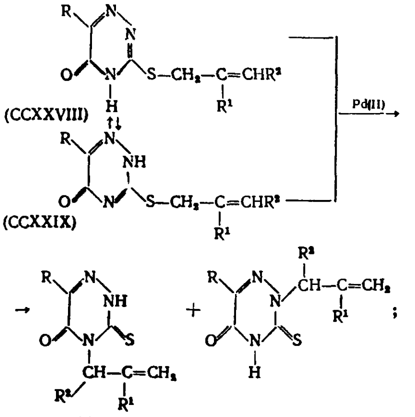


(CCXXVI) (CCXXVII)

Thus the *S*-allyl thioimidate (CCXXVI) is converted quantitatively into the *N*-allylthioamide (CCXXVII) in the presence of a bivalent palladium salt, while the usual thermal reaction (150 °C, decalin) leads only to the product of the isomerisation with respect to the double bond in the allyl group. The reaction mechanism proposed by the authors[147] includes the formation of a six-membered intermediate analogous to that presented in Scheme 21.

The Cope thiaza-rearrangement of 3-allylthio-4*H*-1,2,4-triazin-5-one (CCXXVIII) and 3-allylthio-2*H*-1,2,4-triazin-5-one (CCXXIX), catalysed by palladium(II) complexes, leads to a mixture of the thiones (CCXXX) and (CCXXXI) as a result of the tautomeric equilibrium (CCXXVIII) ⇄ (CCXXIX)[146,147] (Scheme 22).

Scheme 22



(CCXXVIII)
(CCXXIX)
(CCXXX) (CCXXXI)
R=H, Ph, CH_3; R^1=H, CH_3; R^2=H, CH_3.

During the preparation of the manuscript, a number of studies of the mechanism and synthetic use of the aliphatic[148–151] and aromatic[152–155] Cope 3-aza-rearrangements have been published. The Cope 2-aza-rearrangement has been investigated in relation to the cyclisation of *N*-acyliminium salts[156,157] and a series of oxazoline derivatives.[158] The fairly rare Cope 1-aza-rearrangement, achieved under the conditions of flash vacuum thermolysis, has been described.[159] The Cope oxaza-rearrangement has been investigated[160–162] and the thiaza-rearrangement has been used to synthesise condensed thiazole systems[163–164] and also for the synthesis of the indole ring.[165,166]

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Thermotropic Liquid Crystal Polymers with Mesogenic Groups in the Main Chain

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The present state of the synthesis and studies of the structure and properties of thermotropic liquid crystal polymers and copolymers with mesogenic groups in the main chain is examined and the thermodynamic and structural principles of the identification of the polymeric mesophases as well as the influence of the chemical structure of the mesogenic blocks and flexible spacers on the mesomorphic properties of the polymers are discussed.
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I. INTRODUCTION

The interest in the liquid crystal state of polymers which has arisen in the last decade is due to a large extent to the possibility of obtaining ultrastrong highly modular fibres based on polymers exhibiting mesomorphic properties.[1-9] In addition, the study of the nature of the polymeric liquid crystal (LC) state is of independent interest. The lyotropic mesomorphism of polymers has long been known and has been thoroughly investigated; the principal results obtained during the last 20 years in this field have been surveyed in a monograph.[1] Thermotropic LC polymers have been discovered recently and the main direction of studies in this field has been associated with the investigation of the LC state of polymers with mesogenic groups in the side branches.[5,6-8,10] The main idea underlying the creation of such polymers has been the combination of properties characteristic of polymers (including their ability to form films and fibres) with the properties of low-molecular-weight LC compounds. The LC properties were manifested only when the behaviour of the side chains is relatively autonomous. This means that the structural transformations occurring in such polymers at the level of mesogenic groups need not necessarily be associated with the behaviour of the main chain. The mesomorphic properties of such polymers can be in many respects similar to the properties of low-molecular-weight liquid crystals: indeed it has been found that the differences between the electro-optical properties over a wide range of polymers are quantitative but not qualitative.[10]

When the mesomorphic properties of polymers are determined by the structure of the main chain, the differences between the low-molecular-weight liquid crystals and polymers are qualitative, since the structure of the mesophase is found to be related to the macroconformations of the molecules. The LC state of linear polymers is directly related to the anisotropy of the properties induced by the chain structure of the molecules. It would seem that the presence of long chain molecules should give rise to the possibility of the appearance of the LC state in the majority of polymeric systems. Nevertheless the existence of structures exhibiting order intermediate between the types of order which obtain in the crystalline and isotropic states does not always justify the inclusion of such structures among LC structures. Such structures obtain in polyphosphazenes, in polytetrafluoroethylene, in polyethylene at a high pressure, and also on fusion of orientationally-crystallised flexible-chain polymers.[11] A common feature of such structures is a pseudo-hexagonal packing of the chains arising as a result of the appearance of the rotational degree of freedom around the long molecular axis. It is known that such "rotational-crystalline" states occur in many low-molecular-weight compounds[12] (for example, in normal hydrocarbons), and yet such compounds are not classified as liquid crystals. According to Wunderlich's classification, the mesomorphic structures occurring in flexible-chain polymers belong to the category of crystals with elements of conformational disorder.[11]

Thus the chain structure of polymeric molecules is not a sufficient condition for the manifestation of LC properties characterised by the presence of a high degree of orientation order in combination with total or partial absence of positional order.[13]

Orientational order occurs to the maximum extent in complex aromatic polyethers containing only *para*-substituted benzene rings. However, the high anisometry of the molecules increases the stability of the crystal lattice, so that the region in which the mesomorphic properties are manifested lies above the chemical decomposition temperature. One of the ways of reducing the melting point involves the introduction of asymmetric groups or substituents in the *ortho*- and *meta*-positions in the polymer chain,[14] which hinders the packing of the macromolecules in the crystal and lowers appreciably the melting point. The occurrence of mesomorphism in such systems is caused by the rigidity of the polymer chain, which in many respects engenders a similarity between the aromatic polyethers and lyotropic LC polymers such as aromatic polyamides. The high equilibrium rigidity of such polymers results in the appearance of the isotropic state only in the presence of a solvent, i.e. for truly rigid-chain polymers thermotropic mesomorphism is impossible.

According to Flory's theory,[15] which describes the orientational ordering of solutions of rigid-chain polymers, there is a maximum critical axial ratio $p = l/d$ (where l is the length of the molecule and d its diameter) above which the isotropic phase is absolutely unstable in the absence of solvent. The concept of the critical axial ratio, introduced for absolutely rigid rodlike molecules, retains its significance in the description of the ordering in a solution of freely jointed chains,[16] and the quantity $p = A/2d$ represents the anisometry of the

Kuhn segment having a length *A*. Thus the anisometry of a section of the chain with a length of the order of *A* is a criterion of the possibility of the appearance of thermotropic mesomorphism: thermotropic behaviour is observed for sufficiently flexible chain polymers for which the condition $A < 2pd$ holds. The increase in the molecular diameter by the introduction of asymmetric substituents or benzene rings in the *ortho*- and *meta*-positions can entail the complete loss of capacity for crystallisation and also the suppression of LC properties.

One of the most convenient methods of regulating the mesomorphic properties involves the introduction of flexible sections (spacers) into the mesomeric skeleton of the macromolecule. Thermotropic LC polymers, whose mesomorphic properties are determined by the structure of the main chain consisting of rigid mesogenic (*R* = rigid) and flexible (*F* = flexible) fragments (*RF*-polymers) constitute systems with a specific combination of the properties of flexible-chain polymers and low-molecular-weight liquid crystals. The synthesis of *RF*-polymers has given rise to a series of fundamentally new problems for both the physics of liquid crystals and for the physics and chemistry of polymers.

The principal problem among those described involves the elucidation of the relation between the thermotropic mesomorphism of polymers and the LC state of low-molecular-weight compounds, whose nature has been fairly thoroughly investigated.

This problem has the following aspects: is there a possibility of the classification of a structural type of polymeric mesophases on the basis of the classification of low-molecular-weight compounds; how are the properties of the polymers related to the properties of low-molecular-weight model compounds and how does the molecular-weight (MW) of the polymer influence its mesomorphic properties and for what values of MW are the specific features of the LC state realised; to what extent can the ideas and methods of study traditional in the physics of polymers be applied to thermotropic LC polymers.

This review analyses the studies of the synthesis and properties of *RF*-polymers in which the questions formulated above have been reflected; important fields such as electro-optics,[17] rheology, mechanical properties,[18,19] and dielectric properties have remained outside the framework of the review, since the study of these aspects of the thermotropic mesomorphism of *RF*-polymers is only just beginning.

II. CLASSIFICATION AND IDENTIFICATION OF THERMOTROPIC LIQUID CRYSTALS

Liquid crystals can be divided into three main types: nematic, cholesteric, and smectic.[20] In nematic liquid crystals the centres of gravity of the molecules are distributed at random and long-range order is observed only with respect to their orientation (Fig.1*a*). The cholesteric mesophase is illustrated schematically in Fig.1*b*. The centres of gravity of the molecules lie in layers without any order and in each layer, the director (i.e. the vector characterising the preferential direction of the long molecular axes) is located in the plane of the layer. On passing from one layer to the next, it rotates by a small angle and a structure with a helical order is formed overall. Smectic liquid crystals, where the centres of gravity are located in layers but the director is no longer in the plane of the layer, forming an angle with the latter, are the most ordered (Fig.1c). The thermodynamic and structural aspects of smectic mesomorphism have been described in two communications.[21,22]

The knowledge of the type of mesophase makes it possible to infer the behaviour of the substance as a function of the external conditions (temperature, pressure, and external field strength). The main question which arises in the study of newly synthesised LC compounds is therefore related to the elucidation of the type of mesophases formed by the given compound and also to the determination of the temperature limits of their existence.

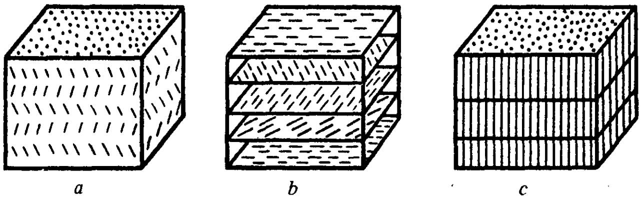


Figure 1. Structural types of mesophases: *a*) nematic; *b*) cholesteric; *c*) smectic.[20]

One of the commonest methods for the determination of the type of mesophase involves the observation of the optical textures of the liquid crystals in polarised light. A specific type of optical texture is associated with the behaviour of the director in the layer of the preparation, which is specific to the given type of liquid crystal. All the textures of LC compounds observed hitherto have been compiled in an atlas.[21] The most reliable identification method is X-ray diffraction, whose foundations in relation to low-molecular-weight liquid crystals have been described in a review;[23] the application of the diffraction methods in the study of mesomorphic polymers has been described by Blumstein.[3] The use of the given method for the identification of mesophases formed by *RF*-polymers is limited owing to the difficulty of obtaining specimens with a homogeneous orientation in a magnetic field.[24–26]

The foundations of the classification of the structural types of mesophases based on calorimetric data have been laid by Barall and Jonson,[27] who examined the ratio of the entropy of their transition from the LC state to the isotropic liquid melt (LC–I) ΔS_i to the overall entropy change in all the transitions undergone by the liquid crystal ΔS_T (this includes the polymorphic transformations in the crystalline phase). It was found that this quantity ($\Delta S_i/\Delta S_T$) is usually small for the nematic phase (of the order of 10^{-2}), while for the smectic phase it is an order of magnitude higher. Analysis of the thermodynamic parameters of the transition showed that calorimetric data can be used for the identification of liquid crystals.

The study of the phase equilibria in mixtures of LC compounds is an extension of the identification method. It is based on the hypothesis that two components can be infinitely miscible when their mesophases are isomorphous. For low-molecular-weight liquid crystals, there are extensive theoretical and experimental data concerning the character of the coexistence of the phases in binary mixtures.[28] The application of the given method to the investigation of polymers has been described in a series of recent studies.[29–31]

For polymeric mesomorphic systems, the problem of identification is greatly complicated, because so far there have been no classifications of polymeric liquid crystals which could satisfy investigators. For this reason, in most studies the authors either use the existing classification for low-molecular-weight compounds or they refrain from any definite conclusions about the type of mesophases. Furthermore, in the identification of polymeric liquid crystals there is a possibility that complications may arise due to kinetic causes, because observations are carried out under conditions remote from thermodynamic equilibrium. Thus the principal concepts accumulated in the study of low-molecular-weight compounds can be applied to the study of the mesomorphism of polymers only with caution since the nature of the polymeric mesophases may differ greatly from that of the low-molecular-weight liquid crystals.

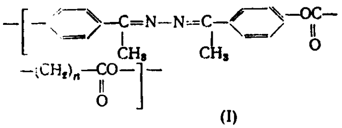
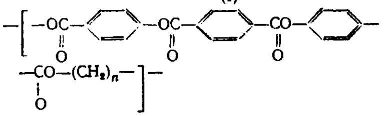
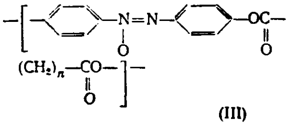
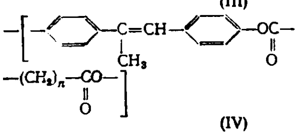
III. THE ROLE OF FLEXIBLE SPACERS IN THE ORDERING OF LIQUID CRYSTAL POLYMERS

In 1975 de Gennes predicted the possibility of the existence of an enantiotropic nematic phase in polymer systems formed by linear flexible macromolecules containing mesogenic groups in the main chain.[32] The synthesis and mesomorphic properties of such polymers were reported at the same time.[33] Subsequently the above investigations developed in the USA, France, the USSR, and the Federal Republic of Germany, which led to the synthesis of tens of *RF*-polymers.[4,34]

According to Flory's theory,[35] for any flexible chain polymer the first (formal) crystallisation stage consists in the cooperative orientational ordering of the polymer chain. This state of orientational order can, however, be thermodynamically unstable in relation to the crystalline phase, which leads to spontaneous crystallisation. This process, leading to a "parallel arrangement" of the chains, corresponds to monotropic LC behaviour. The polyesters synthesised by Roviello and Sirigu are capable of forming an enantiotropic LC phase.[33,36]

The method of synthesis of *RF*-polymers is distinguished by an appreciable flexibility, since wide-scale variation of the chemical nature and molecular parameters of the spacers and mesogenic blocks has been postulated. Aliphatic polyenes of 4,4'-dihydroxy-αα'-dimethylbenzylideneazine with $n = 8$, 10, and 12 carbon atoms in the spacers [Table 1, compound (I)] have been investigated.[33] X-Ray diffraction studies have shown that these polymers are partly crystalline. With the aid of differential scanning calorimetry (DSC) and optical studies, it has been established that the polymers exhibit a first-order transition, which may be associated with the fusion of the crystal structure and also a transition from the LC state to the isotropic state. Comparative studies on the thermodynamic properties of polymers of different chemical nature and model low-molecular-weight compounds demonstrated an appreciable difference between the molar entropies of the LC–I transition.[36,37] For the low-molecular-weight models, this quantity was $\Delta S_i \cong 3$ J mol^{-1} K^{-1}, while for the polymers $\Delta S_i = 13$–16 J mol^{-1} K^{-1}. It has also been observed that ΔS_i is almost independent of the length of the flexible fragments, which has been attributed to the use of the representation of the nematic phase where the disordered flexible part of the chains behaves like an isotropic liquid, i.e. the chains are not involved in the formation of orientational order and can be regarded as solvent molecules. The same conclusions have been reached by other investigators[38] in the study of the temperature dependence of the molar volumes of a series of polymers with flexible spacers of different lengths. The contribution of aliphatic chains to the molar volume proved to be close to the molar volume of amorphous polyethylene, which supports the hypothesis of a disordered conformation of flexible spacers in the nematic phase. However, this conclusion must be made with caution, since the molar volume is not very sensitive to small conformational changes. The conformational state of spacers in different phase states for polymers based on terephthaloylbis(4-hydroxybenzoic) acid [Table 1, compound (II)] has been determined by IR spectroscopy.[39,40] Despite the fact that the conformational composition of the polymers in the LC and isotropic states is almost the same, the flexible-chain spacers in such polymers are partly oriented, i.e. play a definite role in the establishment of the LC order. The orientational order of the flexible sections Q_F is probably related to the redistribution of the rotational-isomeric forms in the LC state compared with the isotropic state. The parameter of the orientation of the mesogenic sections Q_R[†] is different from Q_F and $Q_R > Q_F$. When the length of the spacer is altered, Q_F hardly changes, which indicates a decisive contribution of the intermolecular interactions in the mesogenic sections of the macromolecule. It has been shown that Q_R and Q_F change in the temperature range corresponding to the existence of LC order; under these conditions, Q_R diminishes faster than Q_F, which is due to the temperature dependence of the intermolecular interaction in the mesogenic sections of the macromolecule.

Table 1. Chemical structures and transition temperatures of certain types of *RF*-polymers.

Structure of monomeric unit	*n*	Transition temperature, °C*	Refs.
 (I)	10	*C* 208 *N* 322 *I*	[33]
 (II)	10	*C* 223 *S* 297 *I*	[34]
 (III)	10	*C* 119 *N* 165 *I*	[41]
 (IV)	12	*C* 200 *I* (on heating), *I* 177 *N* 172 *C* (on cooling)	[49]

*C = crystalline phase, N = nematic phase, S = smectic phase, I = isotropic phase; the corresponding transition temperatures are shown between two symbols representing the phases.

[†] The order parameter $Q = \langle(3\cos^2\theta - 1)/2$, where θ is the angle between the rigid section of the chain (or a segment of the flexible fragment) and the anisotropy axis.

The temperature dependence of the order parameter of the polymer based on 4,4'-dihydroxy-2,2'-dimethylazoxybenzene and decamethylene glycol [Table 1, compound (III)] has been determined.[41] The authors note the unusually high order parameter in the transition to the isotropic state for the polymer compared with the low-molecular-weight nematic compound having the initial structure. For the given polymer, Q_R and Q_F vary in parallel and are almost identical. The transition from the isotropic to the LC state is accompanied by a sharp conformational alteration in the spacers: in the LC phase, they have the straight-chain conformation.

The results presented demonstrate the possibility of the operation of two different mechanisms of the ordering of the *RF*-polymers: in the first case, the stability of the mesophase is determined mainly by the intermolecular interaction of the mesogenic fragment and $Q_R > Q_F$, while in the second $Q_R \cong Q_F$, which indicates the decisive role of the macromolecular order. The second variant presupposes the virtually complete ordering of the flexible fragment.

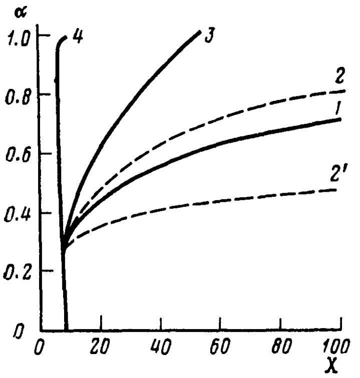


Figure 2. Phase diagram for the system of *RF*-macromolecules; α = volume fraction of flexible fragments; X = length of monomeric unit; flexibility parameter f_0; 1) 1.0; 2) and 2') 0.8; 3) 0.6; 4) 0.4.[42]

The role of the flexible spacers in the orientiational ordering has been examined in a number of studies.[42,43] On the basis of the Flory model for *RF*-polymers,[44] account has been taken of tendency of the LC phase for the flexible fragments to become oriented along the anisotropy axis. One of the most interesting results of this investigation is the conclusion that anisotropic phases of two types can exist as a function of the relative length of the flexible spacers and their rigidity. Fig.2 presents the phase diagram. The flexibility of the spacers f_0 is defined by the equation[35]

$$f_0=\frac{(z-2)\cdot\exp(-\varepsilon/kT)}{1+(z-2)\exp(-\varepsilon/kT)},$$

where z is the coordination number of the lattice and ε the difference between the free energies of the *trans*- and *gauche*-conformers. For an undiluted polymer, the conditions governing the stability of the isotropic phase is the inequality $f_0 > 0.63$. Curve *1* has been obtained without taking into account the finite flexibility of the flexible fragment. The nematic phase is thermodynamically stable in the region to the right of curve *1*. Curve *2* consists of two branches (*2* and *2'*), which corresponds to the fact that, for $f_0 = 0.8$ and also for any $f_0 > 0.63$, there is a possibility of an additional phase transition between two anisotropic phases: a highly ordered phase stable for low values of α and a phase with little order, which is stable for high values of α. When f_0 diminishes, the region of stability of the low-order anisotropic phase shifts towards higher values of α, disappearing at $f_0 = 0.63$. According to Flory,[35] when $f_0 < 0.63$, order obtains even for α = 1 (curves *3* and *4*).

Thus, for sufficiently rigid spacers, the behaviour of this system does not differ from that of a melt comprising rigid rods. For fully flexible spacers, there is a possibility of forming a low-order LC phase, and finally, for spacers with intermediate flexibility, either a highly ordered phase in which the flexible spacers participate in the overall ordering process or a low-order phase in which the spacers play the role of a solvent can be formed depending on the length of the spacers.

This result has been obtained in a somewhat different form by Birshtein and Kolegov,[45–47] who showed that, for polymer solutions containing *RF*-macromolecules, anisotropic phases of two types can exist: in the first case the ordering develops at the level of rigid segments and the chain retains overall the structure of a disordered coil (segmental ordering); in the second case the chain as a whole is ordered and intermolecular interactions ensure the loss of internal flexibility (macromolecular ordering). The occurrence of one or other type of ordering depends on the concentration of the rigid blocks in the solution and also on the mechanism of the flexibility. For the intermediate case of non-freely-jointed rigid blocks, an increase in the concentration of the solution initially entails a transition to the LC state by the segmental mechanism and only then, at high polymer concentrations, does macromolecular ordering occur.

Thus the main difference between the mesomorphisms of polymers and low-molecular-weight liquid crystals reduces to the possibility of the cooperative behaviour of the monomeric units, which depends in a specific manner on the chemical nature of the mesogenic fragments, on the length and nature of the flexible spacers, and also on the way in which they are joined to the mesogenic group. For this reason, the identification of the type of polymeric mesophase must include an analysis of the type of ordering on passing from the isotropic to the LC state. The occurrence of a particular type of ordering in the polymer system is, however, inevitably accompanied by the superposition of kinetic effects, which can greatly increase the uncertainty in the interpretation of the experimental results. The separation of the thermodynamic effects in the I–LC transition constitutes an interesting and important problem whose solution would be a major step towards the possibility of the technological use of *RF*-polymers.

The need to take into account the kinetics of the phase transitions of *RF*-polymers follows from ideas common to flexible-chain polymers, according to which there exist appreciable differences between the mechanisms of the fusion of flexible linear macromolecules and small rigid molecules.[48] These differences are associated with the decisive role of the conformational transformations in the phase transitions of flexible-chain polymers. For this reason, the thermodynamic parameters obtained in the study of phase transitions refer in most cases to the so-called irreversible fusion, i.e.

to fusion under conditions different from those in thermodynamic equilibrium.# The polymer (IV) (Table 1, $n = 12$), which exhibits monotropic mesomorphism, has been investigated.[49] Specimens of the polymer which have not undergone a preliminary heat treatment exhibited a "fictitious" enantiotropic mesomorphism. When the specimens were annealed, the melting point approached the equilibrium value, which proved to be higher than the temperature of the transition to the isotropic melt for the non-annealed specimens. Thus the LC behaviour is manifested by this polymer only under conditions remote from thermodynamic equilibrium. The equilibrium melting point of the polymer (II) (Table 1, $n = 10$) has been determined[50] and has been found to be appreciably higher than the observed melting point. Evidently, in order to understand the nature of the mesomorphism of the *RF*-polymers and also to discover a relation between chemical structure and mesomorphic properties, it is essential to know the equilibrium thermodynamic characteristics of the transition from the crystalline to the LC phase and of the LC–I transition.

Studies of the thermodynamic properties of polymers based on terephthaloylbis(4-hydroxybenzoic) acid[51] in dilute solution have shown that the behaviour of their *RF*-polymers is analogous to the behaviour of the usual flexible chain polymers, since the size of the Kuhn segment does not greatly exceed the size of the repeat unit. Studies on the conformations of the *RF*-macromolecules by measuring the magnetic double refraction established that, in a dilute solution and also in an isotropic melt, the molecules exist in coiled conformations.[52] The Cotton–Mouton constants for model low-molecular-weight compounds, *RF*-polymers, and flexible-chain polymers proved to be of the same order of magnitude and at the same time one–two orders of magnitude less than for aromatic *para*-polyamides and DNA.

Studies on the thermodynamic parameters of the I–LC transition of the polymer (III) ($n = 10$) with different molecular weights showed that ΔS_i increases sharply with increase of the MW, which indicates an increase of the contribution of the flexible spacers to the disordering process[53] (Fig.3). At the same time, the dependence on MW reaches saturation after the attainment of the MW corresponding to approximately 6–8 repeat units, i.e. the cooperative nature of the behaviour of the repeat units does not extend to the entire macromolecule. For high-molecular-weight specimens, the form of the ^1H NMR line for the nematic and crystalline phases was the same,[41] while for oligomeric specimens the spectra of the nematic phase were characterised by dipole splitting typical of homogeneously oriented nematic single crystals. For specimens with a high MW, a structural model of the "multidomain" type, postulating the existence of a marked spatial inhomogeneity, whose main source is the breakdown of orientation (disclination), has been proposed. It is natural to assume that the correlation radius of the orientation of the high-molecular-weight specimens does not exceed the length of 6–8 repeat units, which corresponds to the degree of polymerisation for which the dependence of ΔS_i on the MW reaches saturation. On the basis of magnetic double refraction data, thermodynamic studies, and NMR spectroscopy, it has been concluded that the I–LC transition in oligomeric specimens ($M_n = 1700$–4000) is characterised by a sharp conformational transformation of randomly coiled chains into chains, which are extended to a high degree. In the study of the thermodynamic properties of the *RF*-polymer combined with the measurement of the order parameter in the LC–I transition in the monomer–dimer–polymer series, similar results were obtained[54] (Table 2), and yet the authors nevertheless concluded that the polymeric mesophase has an intermediate degree of order, since, despite the fact that the order parameter of the polymer ($Q = 0.6$) is appreciably higher than for the monomeric compound, it is nevertheless insufficiently high to represent the nematic phase as a set of fully extended chains. The authors assume that, for purely thermodynamic reasons, the system of randomly packed chains undergoes a first-order transition to a nematic phase with an intermediate order.[55]

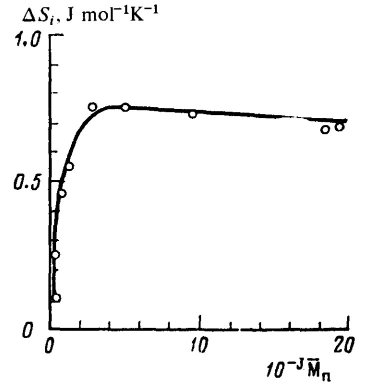
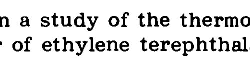


Figure 3. Dependence of the entropy of the LC–I transitions ΔS_i on the molecular weight of the polymers (III) (Table 1); ΔS_i has been referred to the fraction of rigid groups in the main chain.[53]

Table 2. Thermodynamic parameters of the LC–I transition for a nematic polymer, monomer, and dimer.[54]

Specimen*	T, °C	ΔH, kJ mol^{-1}	ΔS, J mol^{-1}K^{-1}	Q
Monomer C_5H_{11}—R—C_5H_{11}	79	0.74	2.09	0.37
Dimer C_5H_{11}—R—$(CH_2)_{10}$—R—C_6H_{11}	148	3.52	8.37	0.49
Polymer —[—R$(CH_2)_{10}$—]— (V)	215	6.53	13.4	0.6

*R =

$$-O-C_6H_4-\underset{\underset{O}{\|}}{C}O-C_6H_4-O-$$

In a study of the thermodynamic properties of the copolymer of ethylene terephthalate with *p*-hydroxybenzoic acid, Krigbaum[56] reached the same conclusions. He showed that, even when, as suggested by Vol'kenshtein,[57] a correction associated with the torsional vibrations (on the assumption that they are fully excited in the nematic and isotropic phases) is introduced into the expression for the free energy, $\Delta S_i/\Delta S_T$ remains approximately 0.45, which is appreciably higher than the experimental value for the polymer investigated ($\Delta S_i/\Delta S_T = 0.11$). It was therefore suggested that

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According to Wunderlich's terminology,[48] irreversible fusion is understood as transition from a metastable crystalline phase to a supercooled isotropic or LC phase and also as fusion accompanied by the superheating of the crystal. Here we employ the concept of irreversible fusion in its first meaning.

in the nematic phase the parameter f_0 is non-zero, i.e the mesophase is characterised by the presence of defects in the form of correlated bends in the chain. Thus the ratio $\Delta S_i/\Delta S_T$ deduced from the lattice model of the nematic phase with allowance for the modification mentioned above decreases from 1 to 0.59 or, when the contribution of the torsional vibration approaches the values calculated from polyethylene,[57] from 0.45 to 0.26. Furthermore, in the lattice model no account is taken of the contribution of the entropy change associated with the increase in volume on fusion. Allowance for this contribution should further diminish the $\Delta S_i/\Delta S_T$ predicted by the theory.

The study of Ianelli et al.[58] was devoted to the determination of the ratio $\Delta S_i/\Delta S_T$ for the polymer (IV) (Table 1) with n = 7 and 9–12 CH_2 groups in the spacers. The authors began with the hypothesis that the value of ΔS_i determined from direct calorimetric measurements correspond to equilibrium. ΔS_T was determined by studying the melting point depression of the polymers with formation of an isotropic melt in the presence of a low-molecular-weight solvent. The ratio $\Delta S_i/\Delta S_T$ amounted to 0.15–0.17 for even values of n and to 0.07–0.09 for odd values, which implies significant differences between the ordering mechanisms for polymers with odd and even numbers of carbon atoms in the spacers. ΔS_T for polymers is usually represented as the sum of three contributions:[59]

$$\Delta S_T = \Delta S_{\text{pos}} + \Delta S_{\text{or}} + \Delta S_{\text{conf}}$$

associated with the positional, orientational, and conformational disordering. For flexible-chain polymers, ΔS_{conf} exceeds all the remaining contributio s to ΔS_T; thus ΔS_{conf} amounts to 75% of the total entropy change for polyethylene[60] and to 65% for poly(ethylene terephthalate).[61] There are no data at present which would make possible analogous calculations for *RF*-polymers, but it is reasonable to suppose that in this case too the contribution of ΔS_{conf} to ΔS_T is decisive. The quantity ΔS_T calculated for each rigid group in the chain obeys the general rule for linear flexible-chain polymers (Table 3), which means that the nature of the isotropic melt for *RF*-polymers is the same as for flexible-chain polymers, which agrees well with the results of magnetic double refraction measurements.[52] Since ΔS_T calculated for each rigid group of the chain in *RF*-polymers is 6–8 J mol^{-1} K^{-1}, presumably the fusion of flexible-chain polymers and *RF*-polymers has the same character. If the conformational contribution to ΔS_T is decisive, the parameter $\Delta S_i/\Delta S_T$ can be regarded as a structural characteristic reflecting the degree of macromolecular order of the polymer chains in the LC phase.

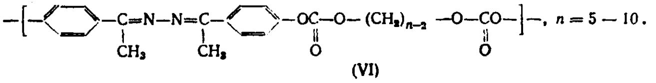
The important role of the macromolecular order is manifested in the change of the thermodynamic properties in homologous series of polymers.§ Differences in the character of the changes in the parameters of the LC–I transition in the homologous series of monomeric, dimeric, and polymeric liquid crystals have been discovered.[62] In the homologous series of monomeric compounds, the usual variation of the mesomorphic properties with increase of the length of the alkyl groups is observed. For certain intermediate lengths, there is a transition from the nematic to the smectic mesophase accompanied by a sharp increase of the clarification entropy; the even–odd effect is most striking for the first homologues and becomes smoothed out with increase of the number of CH_2 groups in the aliphatic components. For the dimer, ΔS_i oscillates about the mean value intermediate between the ΔS_i for the polymer and the monomer and the even–odd alternation becomes more marked on moving from the lowest to the highest homologues (Fig.4). For the polymer, the even–odd alternation is very pronounced and, for all the even and all the odd homologues, the ΔS_i are almost identical. The pronounced even–odd effect for the polymers can be explained by the stronger relation, than in the low-molecular-weight liquid crystals, between the molecular structure of the aliphatic components and the mesomorphic properties. Two different types of ordering, observed for the polymers (III) with aliphatic spacers containing 2–14 carbon atoms, have been described.[63] The first type of ordering has been established for polymers with an even number of carbon atoms (n = 4, 6, 8, 10, 14) and the second for polymers with odd n = 5, 7, 9, 11, 13. The first type is characterised by a higher order parameter $Q = 0.75$ at the clarification point than the second, for which $Q = 0.59$. A high degree of order is achieved as a result of the extension of the spacers, which has been demonstrated by analysing the NMR line form.[41] The corresponding differences between the two types of ordering for polymers with even and odd numbers n are exhibited also in the analysis of thermodynamic data and X-ray diffraction data. The authors explained these features in the following way: the probably of the *trans*-conformation is higher for the first three even bonds, starting from the junction point with the mesogenic component. If both ends of the alkyl chain are fixed, the tendency towards an increase of the number of *trans*-conformers extends along the chain in opposite directions. For an even number of bonds (n is odd), interference results in a decrease of the average ratio of the *trans*- and *gauche*-conformers, while for an odd number of bonds (n is even) the ratio of these conformers actually increases.

Table 3. Thermodynamic characteristics of the C–LC, C–I, and LC–I transitions of flexible-chain and *RF*-polymers*.

Polymer	C-LC			LC-I			C-I				ΔS_T per bond	Refs.
	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS	$\Delta S_i'/\Delta S_T$		
(IV), n=7	—	31.7	—	230	2.72	5.44	185	34.4	75.3	0.07	7.5	[58]
(IV), n=10	—	31.8	—	225	7.37	14.8	195	27.3	87.0	0.17	6.2	[58]
Poly(ethylene-terephthalate	—	—	—	—	—	—	280	26.9	48.5	—	9.7	[48]

*T in °C, ΔH in kJ mol^{-1}, ΔS in J mol^{-1} K^{-1}; C–LC and C–I represent transitions from the crystalline to the LC and isotropic states respectively.

The thermodynamic aspects of the even-odd effect for the *RF*-polymers have been investigated in greatest detail by Roviello and Sirigu.[64] Fig.5 presents the dependence of ΔS_i on n for polymers of three types: (I) (Table 1, n = 6–12), (IV) (Table 1, n = 6–12), and



(VI)

In contrast to the polymers (I) and (IV), the polymers of the (VI) series show virtually no even-odd effect. This finding

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§ Here and henceforth the concept of "homologous series" is that of a series of compounds (polymeric or monomeric) which differ from one another by the number of atoms in the flexible regions.

indicates the decisive role of the structure of the flexible spacers in determining the thermodynamic parameters of the LC–I transition. The replacement of the methylene groups in the spacers of the polymers (VI) by oxygen atoms probably lowers the conformational limitations imposed on the structure of the spacers by the nematic ordering. The authors assume that the question of the role of the flexible spacers in the LC ordering still remains open. Indeed, the study of the thermodynamic parameters of the LC–I transition in *RF*-polymers has shown that, since ΔS_i is characterised by an appreciable even-odd effect, the description of the LC order as a set of rigid rods connected by spacers, playing the role of a solvent, is illegitimate. On the other hand, the hypothesis of an appreciable role of the conformational transformations in the LC–I transition conflicts with the absence of a dependence of ΔS_i on *n* for even and odd values of *n*. If, as follows from the study of Martins et al.,[41] the flexible spacers in the LC phase were almost fully ordered, a marked dependence of ΔS_i on *n* should have been observed. It is essential to note that the estimation of the structure of the spacers by ^{1}H NMR involves the correct allowance for the dipolar contributions to the broadening of the lines due to the protons in the aliphatic and aromatic component, which can be achieved only on the basis of a more or less legitimate hypothesis about the conformations of the spacers. Recent results[65] have shown that the order parameter of the alkyl chains in the LC phase is not the same for the external and internal methylene groups (0.4 for the external groups and 0.3 for the internal groups). It is necessary to note that the studies were performed for a polymer with deuteriated spacers, which permitted the absolute determination of the order parameter of the spacers not requiring hypotheses about their conformational state. For this reason, the initial hypothesis of the stability of the complete ordering of the spacers is not sufficiently well founded.

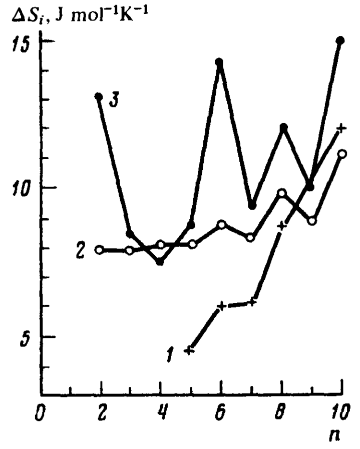

Figure 4. Dependence of the entropy of the LC—I transition ΔS_i on the number of carbon atoms *n* in the aliphatic components for the monomers (curve *1*), dimers (curve *2*), and polymers (curve *3*).[62]

Thus the nematic ordering of the *RF*-polymers differs greatly from the ordering of low-molecular-weight liquid crystals. The macromolecular ordering of the polymers, whose relation involves the cooperative nature of the dynamic behaviour of the mesogenic groups and depends on the chemical structure of the polymer and also on kinetic factors,¶ greatly complicates the task of identifying the polymeric liquid crystals and apparently entails the need to investigate the supermolecular liquid-crystal morphology of the polymers.

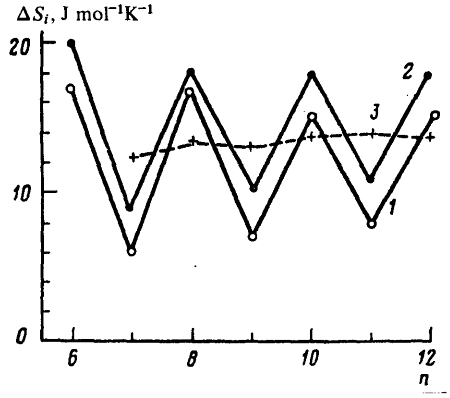

Figure 5. Dependence of the entropy of the LC–I transitions ΔS_i on the number *n* of atoms in the flexible spacers: 1) polymer (I); 2) polymer (IV); 3) polymer (VI).[64]

IV. THE INFLUENCE OF THE CHEMICAL STRUCTURE OF THE MESOGENIC BLOCKS AND FLEXIBLE SPACERS ON THE MESOMORPHIC PROPERTIES OF THE POLYMERS

There are literature data for the synthesis and properties of polymers with flexible spacers of different chemical nature—aliphatic,[33,34,68,69] oligo(ethylene oxide) (OEO), oligo(propylene oxide) (OPO),[70] and disiloxane spacers.[71] The influence of the structure of the mesogenic blocks has been examined in a number of studies.[68,72,73] However, it is as yet difficult to treat from a general standpoint the extensive experimental data concerning the elucidation of the relation between the mesomorphic properties and the chemical structure of the *RF*-polymers. The difficulties in the interpretation are associated with the fact that the mesomorphic properties are influenced by a series of factors such as the composition, inhomogeneity, MW, and the molecular weight distribution (MWD). In the study of polymers with high clarification temperatures, it is essential to take into account

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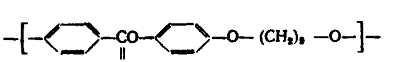
¶ There are no direct indications in the literature that the LC–I transition is non-equilibrium in character. However, certain instances of the monotropic behaviour of the *RF*-polymers have been described.[49,66,67] The occurrence of conformational changes in flexible spacers in the transition to the isotropic melt should lead to the irreversibility of this transition. The small thermal hysteresis and the independence of ΔS_i of the conditions in the heat treatment of the specimens[50] may be a consequence of the kinetic stability of the mesophase and are not an unambiguous proof of its thermodynamic stability.

the possibility of chemical changes which leads to the breakdown of the regulatiry of the chain. Furthermore, the thermodynamic parameters obtained by direct calorimetric measurements do not in most cases correspond to equilibrium, which greatly hinders the elucidation of the relation between the chemical structure and mesomorphic properties.

The influence of the previous history of the polymeric specimens on their mesomorphic properties has been studied in greatest detail by Bilibin et al.,[34] Pashkovskii et al.,[50] Asrar et al.,[74] and Krigbaum and co-workers.[75,76] It has been established that the mesomorphic properties of the polymers depend greatly on the intrinsic viscosity of the specimens $[\eta]$. In the range $[\eta] < 0.4$ dl g^{-1}, the transition temperatures depend greatly on $[\eta]$; the dependence becomes weaker for $[\eta] > 0.4$ dl g^{-1}. Thus, in order to avoid an uncertainty in the interpretation of the experimental data, it is essential to work with specimens having sufficiently high molecular weights. This factor greatly reduces the value of the results obtained in the study of polymers with low $[\eta]$.

The influence of the MWD on the thermal characteristics of the polymers has not been studied in detail, but in a number of communications there are indications that the presence of a broad MWD affects primarily the parameters of the LC–I transition. The synthesis and properties of polymers based on 4-hydroxyphenyl-4-hydroxybenzoate have been described.[77] The transition to the isotropic melt in these polymers is characterised by a broad (50–60 °C) two-phase region, which is a result, according to the authors, of the segregation of the molecules of the specimen with respect to molecular weights in the nematic phase. The influence of the method of synthesis and the purity of the initial components on the properties of the polymers described in the above study[77] has been examined by Krigbaum et al.[76] It was shown that the presence of a broad region in which the isotropic and LC phases coexist is a consequence of the composition inhomogeneity of the polymer specimens, which is caused by the chosen method of synthesis. Krigbaum et al.[76] demonstrated that the correct choice of the methods of polycondensation and purification of the monomers make it possible to synthesise polymer specimens having a narrow two-phase region.

As for low-molecular-weight LC compounds, the mesomorphic properties of *RF*-polymers depend greatly on the chemical structure of the mesogenic blocks. Strzelecki et al.[72] synthesised and investigated the mesomorphic properties of polymers with mesogenic groups containing 2, 3, and 4 benzene rings with nonamethylene spacers: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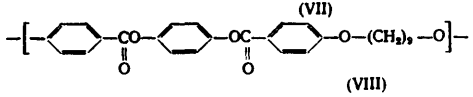
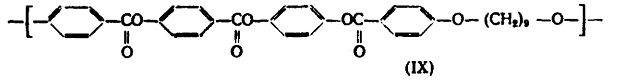
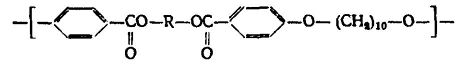
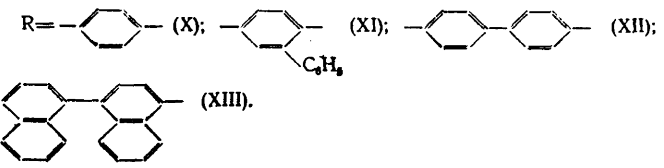

(VIII)


(IX)

The temperatures of the transitions to the isotropic melt for these polymers were respectively 200°, 305°, and 350 °C. The results of the above study[72] have been analysed[74] from the standpoint of the existing theories for low-molecular-weight nematogens, which make it possible to predict the clarification temperature as a function of the chemical structure of the molecules. Using the Flory–Ronca theory,[78] developed for monomeric molecules and taking into account the effects associated with the anisotropy of the molecular shape and with the anisotropy of the intermolecular interactions, the author concluded that the dependence of the clarification temperature T_i on the axial ratio of the rigid blocks is more pronounced for polymers than for the low-molecular-weight liquid crystals. A common conclusion is, however, the claim that existing theories are incapable of predicting the dependence of T_i on the axial ratio of the rigid component of the *RF*-polymers. The influence of the structure of the mesogenic component on the transition temperatures for the polymers (X)–(XIII), having different geometries of the mesogenic blocks and identical structures of the flexible chains, has been studied:[73]



where



It was shown that the clarification temperature and the range of existence of the nematic phase are much higher for the polymers (X) and (XII) than for the polymers (XI) and (XIII) respectively. The changes in the LC properties indicated take place as a consequence of the decrease of the anisometry of the rigid blocks after the introduction of asymmetric substituents.

Thus the character of the influence of the chemical nature of the mesogenic groups on the mesomorphic properties of the polymers is analogous to the influence of molecular structure on the properties of monomeric LC compounds. For low-molecular-weight liquid crystals, there are numerous data describing the relation between the mesomorphic properties and the molecular structure,[79] but there are as yet no criteria which would make it possible to predict the type and range of the existence of the mesophase for substances of a specific chemical nature. One of the most interesting and practically most important is the question of the relation between the structure of the mesogenic blocks and the type of their mesophase. The tendency to generate the smectic phase in low-molecular-weight liquid crystals is associated with the dominant role of the lateral intermolecular interaction compared with the end-face interactions.[5] This postulate is evidently valid also for *RF*-polymers: as can be seen from the data of Strzelecki and Van Lyuen,[80] the increase of the length of the flexible fragments of polymers entails, as for low-molecular-weight liquid crystals, the transition from nematic to smectic mesomorphism. Analogous results have been obtained by Bilibin et al.[81] and it was found that the tendency of polymers to generate the smectic phase is determined in many respect by the tendency of the low-molecular-weight model compounds having an analogous structure to generate this phase. However, the influence of the length of the flexible spacers on the tendency of the *RF*-polymers to generate the smectic phase cannot be explained from the standpoint of the characteristics of the homologous series of low-molecular-weight liquid crystals. A number of polymers based on 4,4′-dihydroxybiphenyl, in which all the even homologues exhibit smectic mesomorphism and the odd homologues exhibit nematic mesomorphism, have been investigated.[74] This indicates the specific role of the flexible spacers in the ordering of the *RF*-polymers.

The most important confirmation of the special role played by the flexible fragments in the generation of LC order in polymers is the marked dependence of the mesomorphic properties on the chemical nature of the spacers. The flexibility of the latter is a decisive factor influencing their clarification temperature. It has been shown that, for polymers with disiloxane spacers, the range of existence of the mesophase is much narrower and the clarification temperature is lower than for the polymer with decamethylene spacers.[71] Table 4 presents the thermodynamic parameters of the LC–I transition for a series of polymers whose rigid groups consist of aromatic triads and the chemical nature and lengths of the flexible spacers are different. For the polymers with disiloxane spacers (XIV), ΔS_i is greater and T_i appreciably lower than for the polymer with decamethylene spacers (XV), which indicates the decisive role of the entropy jump ΔS_i in the LC–I transition. The introduction of the oligo-oxyethylene spacers does not entail an appreciable decrease of ΔS_i compared with polymers containing oligomethylene spacers [(XIV) and (II), $n = 6$]. However, ΔS_i reflects not only the conformational features of the chains in the isotropic phase but also the structural features of the mesophase and for this reason unambiguous conclusions about the influence of ΔS_i on T_i can be made only on the basis of the knowledge of the structure of the LC and isotropic phases. It is of interest to note that, for polymers having spacers containing asymmetric centres (for example, the OOP spacers[70,81]), calorimetric measurements do not allow the determination of ΔH_i and T_i. Polymers with OOP spacers are non-crystallisable but there are no explicit indications of the suppression of their mesomorphic properties. In a number of studies, it has been reported[74,82,83] that polymers with OOP spacers are capable of forming a cholesteric mesophase. For low-molecular-weight nematic and cholesteric liquid crystals, the ΔS_i are virtually identical[25,26] and the significant difference between the thermodynamic properties of the nematic and cholesteric phases of *RF*-polymers can therefore be accounted for solely by the conformational features of the chains in each phase. The conformation of the chains in the cholesteric phase probably does not differ greatly from the conformation of a statistical coil, which explains the absence of a measurable entropy jump in the LC–I transition in polymers with OOP spacers.

Thus the variation of the chemical nature of the flexible spacers influences decisively the mesomorphic properties of *RF*-polymers. The character of the influence of the nature of the flexible components on the mesomorphic properties of the polymers cannot be understood from the standpoint of the traditional ideas about the mesomorphism of low-molecular weight compounds, since the structure of the polymeric mesophase is determined to a large extent by the conformational state of the macromolecules.

V. COPOLYMERS

The study of the properties of copolymers has attracted investigators for a number of reasons. The nematic states in copolymers have a wider region of stability than in the case of homopolymers.[84] It has been shown that LC polymers based on non-mesomorphic components can be obtained by copolycondensation.[85] The synthesis and properties of copolymers containing aliphatic fragments of different lengths have been reported.[38,84] It has been shown that, in terms of its structural and thermodynamic aspects, the mesophase of the copolymers is virtually identical with the mesophase of the homopolymers, which is indicated by DSC and X-ray diffraction data. The phase diagram for copolymers based on 4,4'-dihydroxy-αα'-dimethylbenzylideneazine, containing octo- and dodeca-methylene spacers, is presented in Fig.6*a* [Table 5, compound (XVII)]. The solidus lines (which have the form usual for eutectic diagrams) and the line representing the equilibrium between the nematic phase and the isotropic melt indicate the complete compatibility of the copolymer units in the LC phase. It has been established that copolymers with the equimolar composition have a very low degree of crystallinity and that under certain conditions it is possible to obtain specimens in the nematic vitreous state.

Copolymeric systems with one non-mesomorphic component, which, however, is capable of potential mesomorphism have been investigated[86] [Fig.6*b*, Table 5, compound (XVIII)]. When the content of the non-mesomorphic component is in the range $0 \leq m \leq 75$ mole %, the copolymers exhibit enantiotropic

Table 4. Thermodynamic parameters of the LC–I transitions of *RF*-polymers with different structures of the flexible spacers.

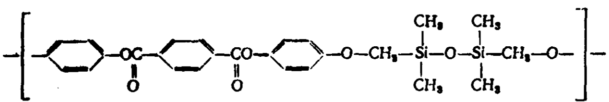
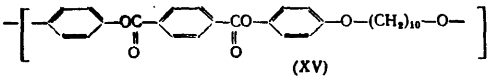
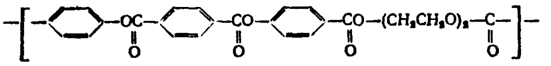
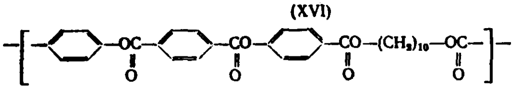
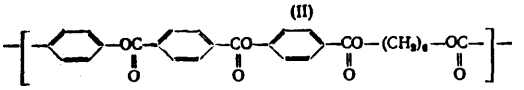
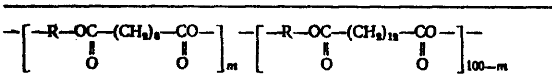
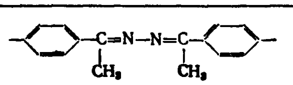
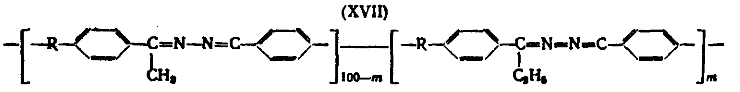
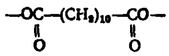
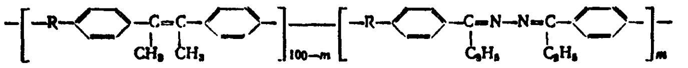
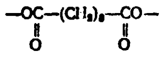
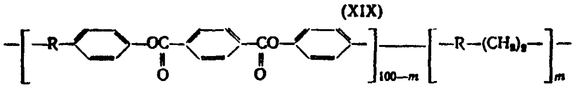
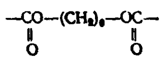
Structure of monomeric unit	T_i, °C	ΔH_i, kJ mol^{-1}	ΔS_i, J mol^{-1} K^{-1}	Refs.
 (XIV)	208	8.0	16.8	[71]
 (XV)	268	2.8	5.0	[71]
 (XVI)	335	7.4	12.2	[81]
 (II)	293	9.3	16.3	[81]
 (II)	347	8.6	13.9	[81]

Table 5. Certain types of mesomorphic *RF*-copolymers.

Structure of copolymer	R	Refs.
 (XVII)		[84]
 (XVIII)		[86]
 (XIX)		[85]
 (XX)		[87]

mesomorphism. When the content of the non-mesomorphic component is greater, there is a possibility of the manifestation of only monotropic mesomorphism in the system. Extrapolation of the thermodynamic parameters for the LC–I transition to the 100% content of the non-mesomorphic component made it possible to determine the "potential" mesomorphic properties of the polymer containing only non-mesomorphic units.† Copolymers with two non-mesomorphic components, exhibiting potential mesomorphism, have been investigated [Fig.6c, Table 5, compound (XIX)].[85] Enantiotropic mesomorphism has been observed in the composition range 35 ≤ *m* ≤ 60 mole %. The manifestation of LC properties by copolymers becomes possible by virtue of the significant expansion of the region of stability of the mesophase. In this sense copolymers play the same role as mixtures of low-molecular-weight compounds with potential mesomorphic properties.

The synthesis of copolymers with a single non-mesomorphic component, which does not exhibit potential mesomorphism, has been described[87] [Fig.6*d*, Table 5, compound (XX)]. In contrast to those examined above, copolymers of this type are characterised by a broad two-phase region corresponding to the LC–I transition, which greatly expands with increase in the fraction of the non-mesomorphic component, which implies that there is partial segregation of the non-mesomorphic component.

Despite the outward similarity of the phase diagram presented in Fig.6 and the diagrams for mixtures of low-molecular-weight liquid crystals, the experimental data for copolymers cannot be understood from the standpoint of the characteristics known for low-molecular-weight systems. Furthermore, the study of the copolymers is complicated by the difficulty of obtaining phase equilibria, which greatly limits the progress in this field. Nevertheless, the need for more far-reaching study of the copolymers is evident because of their great practical importance. Copolymerisation is the most effective method of regulating mesomorphic properties and makes it possible to vary parameters important for applications, such as the degree of crystallinity, the glass point, and the mechanical characteristics of the given articles. From the standpoint of the use of *RF*-copolymers in the industrial manufacture of high-strength highly modular articles, systems analogous to that illustrated in Fig.6d are of greatest interest, since copolymers of this type make it possible to vary within wide limits the rheological characteristics of anisotropic melts.

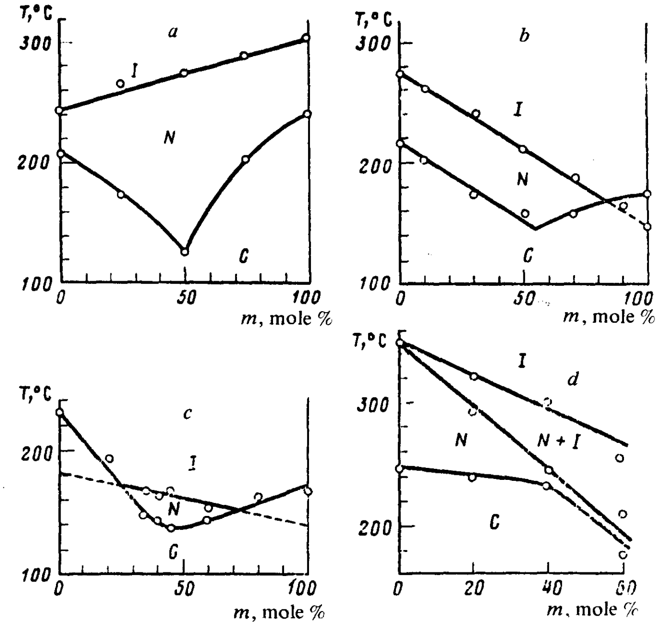


Figure 6. Phase diagrams for the copolymer systems presented in Table 5: *a*) (XVII); *b*) (XVIII); *c*) (XIX); *d*) (XX); *I*, *N*, and *C* = isotropic, nematic, and crystalline phases respectively; *m* = composition of the copolymer; *T* = temperature.[84–87]

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† In this case the term "non-mesomorphic component" does not reflect the mesomorphic properties of the monomeric unit and is used in the sense that the homopolymer containing 100% of the non-mesomorphic units is also non-mesomorphic. Compounds for which the temperature of the transition from the crystalline to the isotropic state is higher than the clarification temperature are potentially mesomorphic.

Analysis of the data presented in the review permits the differentiation of three main trends in the study of *RF*-polymers: (1) the elucidation of the character of the influence of the chemical nature of the repeat unit on the mesomorphic properties of the polymers; (2) the study of the structure of the mesophases; (3) the determination of the relation between the molecular characteristics and the LC properties of the polymer. The value of the results obtained in the study of the structural characteristic features of the mesophases or of the influence of chemical structure on the properties of *RF*-polymers is greatly reduced if there are no corresponding data for the dependence of the mesomorphic properties on the molecular characteristics of the polymers. Nevertheless, whereas the first two research trends are fairly widely represented in the literature, the third is only in the initial stage of its development.

Thus an unambiguous interpretation of the experimental data is possible only for polymers with a rigorously defined composition, chemical structure, molecular weight, and molecular weight distribution.

An important feature of *RF*-polymers is the possibility of macromolecular ordering together with the establishment of orientational order at the level of individual segments. This accounts for the interest in the study of the behaviour of the flexible fragments in the I–LC transition. Many experimental data indicate a high activity of the spacers, which is one of the manifestations of the macromolecular ordering process.

Despite the major advances made in the synthesis and study of *RF*-polymers, the problem of the classification of the types of mesophases for the given system remains unsolved. Identification of the low-molecular-weight liquid crystals permits a comprehensive prediction of the behaviour of the given substance as a function of external conditions. The determination of the analogous characteristics of *RF*-polymers should include, apart from the determination of the type of mesophase at the segmental level, the determination of the geometrical characteristics of the chains in the LC phase, since these parameters in fact determine in many respects the macroscopic properties of the polymer. It therefore appears to be essential to develop research directed to the determination of the macroconformations of the chains of mesogenic polymers in the LC phase.

Linear thermotropic polymers capable of existing in the LC state at temperatures ranging from room temperature to 350–400 °C are known. Naturally such a wide range of the thermal stability of the polymeric mesophases gives rise to extensive possibilities for the application of *RF*-polymers in extremely varied fields of science and engineering. Applied studies of *RF*-polymers are directed mainly to the synthesis of fibres and films with improved strength characteristics and a high thermal stability. More far-reaching investigation of the nature of the LC state will undoubtedly open new pathways to the more extensive employment of *RF*-polymers in science and engineering. Furthermore, the interest in thermotropic linear polymers is of fundamental importance: like the study of monomeric liquid crystals, it has expanded our knowledge of the molecular structure of liquid crystals and the study of polymers deepens our understanding of the analogous features of polymer melts and crystals.

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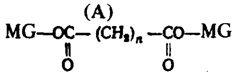
During the preparation of the review for the press, studies of fundamental importance were published. With the aid of the model of rotational-isomeric states,[88] a detailed investigation has been made of the conformational changes in the flexible fragment in the I–LC transition. It has been shown that the behaviour of the spacers during nematic ordering depends on the structure of the groups connecting the flexible fragments to the mesogenic groups (MG). Three types of connection of the spacers to the MG have been examined:

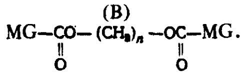
$$\mathrm{MG{-}O{-}(CH_2)_n{-}O{-}MG};$$

(A)



$$\mathrm{MG{-}\underset{\displaystyle O}{\underset{\|}{C}}O{-}(CH_2)_n{-}O\underset{\displaystyle O}{\underset{\|}{C}}{-}MG};$$

(B)



$$\mathrm{MG{-}\underset{\displaystyle O}{\underset{\|}{C}}O{-}(CH_2)_n{-}O\underset{\displaystyle O}{\underset{\|}{C}}{-}MG}.$$

(C)

The connections of the (A) and (B) types are preferred for the establishment of the nematic state, since they ensure highly "extended" spacers and a parallel arrangement of the MG without a significant decrease of the configurational partition function for the system. This explains the high conformational contribution to the overall entropy change ΔS_i for *RF*-polymers with connections of the (A) and (B) types and the fact that ΔS_i for polymeric nematic materials is higher by an order of magnitude than for low-molecular-weight materials. In case (C) the extended state of the spacers is unlikely and nematic ordering is therefore unfavourable. If, however, the nematic state does nevertheless obtain, the conformational contribution to ΔS_i is small, since the conformational structure of the spacers in the isotropic and LC phases is virtually the same. The principal conclusions of Yoon and Bruckner[88] have been confirmed experimentally[89] by ^{2}H NMR for a polymer with connections of type (A). The results of the IR spectroscopic study of the structure of the spacers for polymers with type (C) connections[39,40] also confirmed the theory.[88]

Blumstein[90] and Pashkovskii[91] paid particular attention to the study of the dependence of the parameters of the LC–I transition on the molecular weight taking into account the chemical structure of the end groups of the macromolecules. It has been shown that, in the region of low molecular weights, the structure of the end groups influences strongly the properties of *RF*-polymer specimens. This finding demonstrates the difficulty of interpreting the experimental data obtained in the early studies[68,70] for low-molecular-weight specimens.

Volino et al.[92] studied the structure of solutions of an *RF*-polymer in a low-molecular-weight nematic liquid crystal. Relations were obtained between the order parameter of the polymers Q_{RF} and the degree of polymerisation x. It was shown that Q_{RF} increases with increase in the parameter x, tending to the value of Q for a low-molecular-weight nematic material, which indicates the ideal "incorporation" of the polymer chains in the nematic medium. The data of Volino et al.[92] agree with the theory,[93] where it has been shown that flexible *RF*-polymer molecules can be rigid in the nematic phase, in contrast to the usual flexible-chain or comb-shaped LC polymers.

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Thermal Polymerisation and Oligomerisation of Monomers

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Two competing types of thermal reactions of monomers of different classes, namely oligomerisation and polymerisation, are examined. The characteristics of the formation of the initiating radicals and of low-molecular-weight products (dimers and trimers) and of the inhibition of the thermal polymerisation by radical acceptors have been subjected to kinetic analysis. The mechanisms of the principal pathways in this process and the relations between them are discussed.
The bibliography includes 136 references.

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I. INTRODUCTION

Thermal polymerisation† is the principal type of reactions of monomers; it proceeds exclusively under the influence of heat in the range of relatively low temperatures where the reactions involving the decomposition of the carbon skeleton of the molecule hardly occur. Its products are polymer and low-molecular-weight compounds—oligomers (dimers and trimers) having both linear and cyclic structures.

The importance of this study of thermopolymerisation is determined by practical and theoretical factors. Firstly, thermopolymerisation is an inseparable component of the overall polymerisation process occurring in the industrial isolation of monomers, which leads to the formation of polymer deposits and the breakdown of equipment. Secondly it is one of the methods of synthesis of polymers, for example styrene polymers. For this reason, the knowledge of the detailed features of the mechanism of the thermal reactions of monomers permits a more deliberate and better founded purposeful regulation of this reaction depending on the character of the problems undertaken. The mechanism of the generation of initiating radicals and oligomers, especially six-membered oligomers, is of theoretical interest. As regards the latter, two mechanisms of their formation have been discussed in the literature during a number of years: the synchronous and two-centre (biradical) mechanism.

The aim of the review was therefore to survey and analyse the literature data on the thermal reactions of various representatives of vinyl and acetylenic monomers, to discover the general features of these processes, and to attempt to formulate on this basis a single mechanism of the phenomenon under consideration. The need for the present review arose because, despite the fairly long history of the research into monomer reactions of this type, scarcely any attempts have been made to survey the available literature data which have accumulated during the last 20–30 years. In view of the fact that the cyclo-addition reactions constitute an independent branch of organic chemistry, as regards the latter we shall confine ourselves to conclusions which have a direct bearing on the topic of the present review.

II. MONOMERS OF THE VINYL-AROMATIC SERIES

1. Styrene and Its Derivatives

In the early studies, only the formation of the polymer was investigated. Reactions of both first and second order with respect to the monomer have been reported. The first exact reaction order, amounting to 2.5, was established by Flory[1] and then by Mayo and co-workers[2–5] and an expression has also been found for the rate of initiation:[2]

$$w_i\ (\text{mol litre}^{-1}\text{s}^{-1}) = 1.32\times10^{6}\exp(-121/RT)\,[M]^{3}$$

(here and henceforth M represents the monomer), which agrees well with the equation which we obtained on the basis of Flory's results.[1]

The reaction order obtained has been interpreted in different ways. Thus it has been assumed that the polymerisation is initiated by the radicals formed as a result of a trimolecular reaction of styrene, via a trimeric biradical, or by monoradicals arising from the latter (see Bagdasar'yan,[6] pp.9, 59). However, it has been shown[6,7] that biradicals cannot ensure the propagation of the chain process. This has also been confirmed by the polydispersity of the polymer, amounting to 1.8–2.0,[8] which is characteristic of monoradical initiation. Finally, special generation of the biradicals $C_6H_5\dot{C}HCH_2.$ $.CH_2\dot{C}HC_6H_5$ by the decomposition of the corresponding tetrahydropyridazine only slightly increased the rate of polymerisation of styrene.[9] The trimolecular reaction is regarded as unlikely because of the lack of a kinetic isotope effect in the polymerisation of ββ'-dideuteriostyrene.[10]

A qualitatively new stage in the development of a theory of thermopolymerisation was represented by Mayo's studies,[2,11] in which, together with the polymer, low-molecular-weight products L were detected, the rate of formation of which obeys a second order equation with respect to the monomer:

$$w_L\ (\text{mol litre}^{-1}\text{s}^{-1}) = 1.8\times10^{5}\exp(-95/RT)\,[M]^{2}.$$

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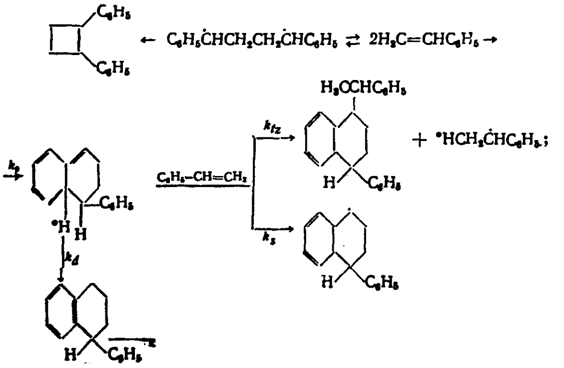
† Henceforth we shall also use the term "thermopolymerisation", since it has become a traditional designation of this phenomenon.

Among the low-molecular-weight products, *cis*- and *trans*-diphenylcyclobutanes (DPCB), 1-phenyltetralin (PT), and 1-phenyl(phenylethyl)tetralin (PPET) were identified.[11-13] On this basis, Mayo proposed a new thermopolymerisation mechanism, according to which the primary product, 1-phenyl-1,2,3,9-tetrahydronaphthalene (PTHN), arising from a bimolecular reaction of styrene of the type of the Diels–Alder condensation, is responsible for the formation of the initiating radicals and oligomers. The set of reactions occurring under these conditions is described by the scheme



The expressions for the rates of initiation (w_i) and trimerisation (w_{tr}) arising from this scheme, i.e.

$$w_i=\frac{k_0k_s[M]^3}{k_d+(k_s+k_{tr})[M]};\ w_{tr}=\frac{k_0k_{tr}[M]^3}{k_d+(k_s+k_{tr})[M]}$$

are consistent with the experimental relations. The DPCB formation reaction is of second order with respect to styrene and is characterised by an activation energy of 104 kJ mol^{-1}.[12] It has been suggested that the high reactivity of PTHN is due to the lability of the hydrogen atom H*.[11,12]

The main evidence for this mechanism is believed to be the presence of the kinetic isotope effect in the initiation stage of the thermopolymerisation of *o*-dideuteriostyrenes,[14,15] the direct identification of PTHN by UV spectroscopy,[16-18] the absence among the reaction products of biradicals generated from diphenyltetrahydropyridazine and phenyltetralin,[19] and the manifestation of an initiating capacity by certain PTHN analogues.[20,21] An additional argument is provided by the ability of styrene dimers to regulate the molecular weight of the polymer;[8,22-24] it has been suggested that this role is played by PTHN.[25,26] Indeed the molecular weight of polystyrene and the concentration of PTHN exhibit an antiparallel time variation,[16,17] while compounds modelling PTHN are capable of playing the role of a chain transferring agent.[20,21]

Among the styrene derivatives, compounds substituted both in the aromatic ring and in the α- and β-positions in the side chain were investigated in the thermopolymerisation reaction. We shall consider initially derivatives of the first type. Data for the polymerisation of methylstyrenes have been published in a number of communications.[27-29] The activation energies for the overall process are 70, 80, and 70 kJ mol^{-1} for *o*-methylstyrene, *m*-methylstyrene, and vinylxylene respectively. Vinylmesitylene does not polymerise even in the presence of initiators. The thermopolymerisation of *p*-methoxystyrene has been investigated.[30] If it is supposed that the overall reaction order is also 2.5, it is possible to obtain an expression for the rate of initiation:

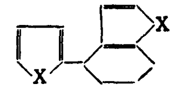
$$w_i\ (\text{mol litre}^{-1}\text{s}^{-1})=4.6\times10^7\exp(-125/RT)\ [M]^3.$$

The rate constant for the initiation of the polymerisation of o-chlorostyrene is described by an expression with the following parameters: E_i = 125 kJ mol^{-1} and A_i = 3.47 × 10^{10} litre^2 mol^2 s^{-1}.[31] For pentafluorostyrene, E_i = 84–92 kJ mol^{-1}.[32] Fairly numerous data are also available for other halogeno- and alkyl-halogeno-styrenes,[33-37] but the lack of information about the polymerisation rate constants precludes the calculation of the rate of initiation. Nevertheless, one may conclude that the variation within wide limits of the activation energies (by 37 kJ mol^{-1}) and pre-exponential factors for the rate constants (by 5 orders of magnitude) for the thermopolymerisation reactions of various styrenes is in the main a result of the variation of the corresponding parameters of the initiation stages.

The thermopolymerisation of styrenes containing substituents in the side chain has been little studied. It has been shown that α-methylstyrene polymerises only at high pressures.[38] Together with the polymer, a linear unsaturated α-methylstyrene dimer has been detected.[39] Only perfluorocyclobutane is formed from αββ′-trifluorostyrene,[40] while α-bromostyryl-1-phenylnaphthalene[41] and various chloro- and fluoro-styrenes are capable only of slow dimerisation.[42]

2. Other Vinyl-aromatic Monomers

The polymerisation of vinylthiophen (VT) and vinylfuran (VF) has been investigated.[44,45] Together with the polymer, a dimer having the structure



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where X = O or S, is formed. Its yield is comparable to that of the polymer. The initiation process is characterised by third order with respect to the monomer, the activation energies being 117 and 125 kJ mol^{-1} for VT and VF respectively. The pre-exponential factors in the expressions for the VT and VF polymerisation rate constants were similar, amounting to 9 × 10^2 litre$^{3/2}$ mol$^{-3/2}$ s^{-1}. The data obtained are consistent with a polymerisation mechanism identical with that proposed by Mayo.

Analysis showed that the observed polymerisation rate constant is almost independent of the monomer concentration and the stage involving the conversion of the intermediate into trimers does not therefore exist. This is confirmed by the observation of only the dimer in the low-molecular-weight fraction,[45] from the yield of which it is possible to estimate approximately the dimerisation rate constant. At 130 °C the latter is approximately 1.6 × 10^{-6} litre mol^{-1}, i.e. is comparable to the rate constant for the oligomerisation of styrene.

The thermopolymerisation of vinylpyridines (VP) has been investigated in a number of studies.[32,46-48] Expressions describing the rate of initiation have been found for 4-VP and 2-methyl-5-VP:[46,48]

$$w_i\ (\text{mol litre}^{-1}\text{s}^{-1})=9.7\times10^{11}\exp(-133/RT)\ [M];$$
$$w_i\ (\text{mol litre}^{-1}\text{s}^{-1})=2.38\times10^{3}\exp(-88/RT)\ [M]^3.$$

The first order observed in the case of 4-VP is open to definite doubt. The surface of the glass probably exerts an influence in this instance, as noted by Onyon.[47] The overall rate constant is independent of the monomer concentration. An initiation activation energy similar to that found for 4-VP has been obtained also for 2-VP.[32] Aminov and co-workers[46,48] give preference to a biradical mechanism, although one cannot rule out the possibility of the formation of an intermediate similar to PTHN.

The thermopolymerisation of vinylpyridinium salts in aqueous solution proceeds via a radical-chain mechanism and the rate of reaction is proportional to $[M]^{2.2}$.[49]

Although the polymerisation of indene has not been subjected to kinetic analysis, nevertheless it has been shown that the rate of this process is lower than the rate of polymerisation of styrene and the degree of polymerisation ranges from 2 to 10, amounting on average to 4–6.[50] The rates of reaction at different temperatures, obtained in different studies, fit satisfactorily on a single linear Arrhenius plot and the activation energy is 94 kJ mol^{-1}.[51–54] There are no literature data for the relative kinetic chain propagation rate constant $k_p/k_t^{0.5}$, where k_p and k_t are the kinetic chain propagation and termination rate constants respectively. We calculated it using the data[54] for the polymerisation of indene initiated by benzoyl peroxide. The required constant was found to be given by the following expression

$$k_p k_t^{0.5}\ (\text{litre}^{1/2}\text{mol}^{-1/2}\text{s}^{-1/2}) = 3.2\times10^2 \exp(-33.6/RT).$$

The dependence of the degree of polymerisation on the initiator concentration (indene peroxide)[55] shows that the molecular weight of the polymer is regulated by chain transfer via the monomer. The calculated transfer constant was found to be 0.1. This can explain the low-molecular-weight of the polymer. The exact concentration-based measurement of the order of the polymerisation reaction with respect to the monomer was not carried out, but, according to an approximate estimate, it should be greater than 2. If it is assumed to be 2.5, then the pre-exponential factor in the expression for the initiation rate constant is 3.8 $\text{litre}^2\ \text{mol}^{-2}\ \text{s}^{-1}$ and the activation energy is 120 kJ mol^{-1}.

According to the data of different workers, the activation energies for the overall polymerisation (numerals designated by an asterisk) and initiation processes involving naphthalene derivatives are respectively 73*,[56] 71*,[32] and 123 kJ mol^{-1} [32] for α-vinylnaphthalene, 129* and 159* kJ mol^{-1} for acenaphthalene,[32] 76* kJ mol^{-1} for β-vinylnaphthalene, and 87* kJ mol^{-1} [56] for 6-vinyltetrahydronaphthalene. Decahydronaphthalene does not polymerise at 100 °C in the course of three days.[56]

If the order of the initiation stage of the polymerisation of α-vinylnaphthalene (α-VN) with respect to the monomer is three, then the rate constant can be calculated from the data of Koton and Kiseleva:[56]

$$k_i\ (\text{litre}^2\text{mol}^{-2}\text{s}^{-1}) = 4\times10^3 \exp(-73.0/RT)$$

(the polymerisation constants taken from Lipatov et al.[57] were used in the calculation).

3. The Kinetics and Mechanism of the Inhibition of the Thermopolymerisation of Styrene by Alkyl Radical Acceptors

The characteristic features of the inhibition of thermopolymerisation exhibit a number of significant differences from the initiated reaction. The relation between the inhibitor concentration and the induction period is usually non-linear.[58–62] The kinetic orders of the acceptor consumption reaction can be both zero[60,63–67] and unity[64,67] and in the former case the rates of destruction of different acceptors can differ by a factor of several tens and can greatly exceed the rate of initiation in the absence of acceptors.[63–69] The products of the thermal and initiated reactions are frequently different.

Thus the high-molecular-weight product formed in the initiated thermopolymerisation of styrene in the presence of quinones is a styrene–quinone copolymer, while the product of the non-initiated process is a styrene homopolymer.[70] The formation of 2 : 1 or 2 : 2 adducts of the monomer and the inhibitor (benzoquinone, sulphur, picric acid),[71,72] in which the dimeric styrene fragment has a linear structure, is a characteristic feature.

Details kinetic analysis of the thermopolymerisation inhibition process has shown[72] that the above features are caused by the reactions of the intermediate arising as a result of a bimolecular reaction of styrene:

$$\begin{gathered}
\text{M} + \text{M} \xrightarrow{k_0} \text{Z}, \\
\text{Z} \xrightarrow{k_d} \text{D}, \\
\text{M} + \text{Z} \xrightarrow{k_{tr}} \text{T}, \\
\text{M} + \text{Z} \xrightarrow{k_s} \dot{\text{R}}, \\
n\,\text{In} + \text{Z} \xrightarrow{k_b} \text{products}, \\
f\dot{\text{R}} + \text{In} \xrightarrow{k_{in}} \text{products},
\end{gathered}$$

where M, D, and T are the monomer, dimer, and trimer respectively, Z is the intermediate, In the inhibitor, n the stoichiometric coefficient, f the acceptance coefficient, and $\dot{\text{R}}$ the initiating radical. According to this scheme, the consumption of the inhibitor is defined by the expression

$$-\frac{d[\text{In}]}{dt} = k_0[\text{M}]^2 \frac{k_s[\text{M}]/f + nk_b[\text{In}]}{k_d + (k_{tr} + k_s)[\text{M}] + k_b[\text{In}]}.$$

Since $k_s[\text{M}]$ is fairly small, we obtain

$$-\frac{d[\text{In}]}{dt} \simeq \frac{nk_0k_b[\text{M}]^2[\text{In}]}{k_d + k_{tr}[\text{M}] + k_b[\text{In}]}.$$

Depending on the absolute values of the individual terms, two limiting cases can occur, where the inhibitor is consumed either in accordance with a zero order law at a rate $nk_0[\text{M}]^2$ and W_i/f or in accordance with a first-order law at a rate proportional to $nk_0k_b[\text{M}]^2/k_d + k_{tr}[\text{M}]$. This agrees with the experimental reaction orders (see above) and also shows that, depending on the conditions and the reaction time, the order may also assume intermediate values (between 0 and 1).

An equation relating the induction period τ to the inhibitor concentration was obtained in the same study:[72]

$$\tau = \frac{[\text{In}]_0}{nk_0[\text{M}]^2} + \frac{k_d + k_{tr}[\text{M}]}{nk_0k_b[\text{M}]^2} \ln \frac{nfk_0k_b[\text{M}]^2}{k_d + k_{tr}[\text{M}]w_i}[\text{In}]_0.$$

Depending on the initial inhibitor concentration, both a linear and a logarithmic relation between τ and $[\text{In}]_0$ can be obtained, which has been observed in practice. Furthermore, the above equation makes it possible to determine the reactivity of the intermediate towards the acceptor {the effective rate constant $k = nk_0k_b[\text{M}]^2/k_d + k_{tr}[\text{M}]$}, the rate of initiation, and the lower threshold of the rate constant for the reaction of the radicals, propagating the kinetic chains, with the inhibitor.

With the aid of this approach, we calculated the effective rate constants k for the interaction of the intermediate with various inhibitors (Table 1). A satisfactory agreement is observed between the values of k calculated from the induction period and from the consumption of the acceptor. A satisfactory agreement was also noted for the rate of initiation w_i and the inhibition rate constant k_{in} found in this way.[72] The constant k for different acceptors varies within the limits of one order of magnitude and has the maximum value for stable radicals. However, there are exceptions: Kolesch's radical# and tetramethyl-p-benzoquinone are consumed at a

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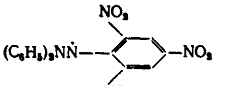
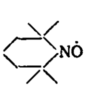
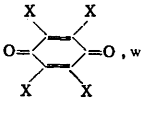
1,3-Bis(diphenylene)-2-phenylallyl (BDPA)—see Pryor et al.[64] (cf.Table 1) (Ed.of Translation).

rate close to the rate of initiation and the interaction with the intermediate does not accordingly occur. It is of interest that, on passing to pentafluorostyrene, such reaction with Kolesch's radical becomes possible (Table 1).

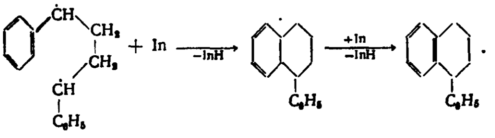
Table 1. The effective rate constants for the reactions of the intermediate with inhibitors.

Inhibitor	t, °C	$10^4 k$, s^{-1}	Method of determination
	Styrene (Ref.72)		
	75	1.67	from consumption of inhibitor
	80	1.67	from τ
Ditto	80	1—2	from consumption of inhibitor
$(C_2H_5OC_6H_4)_2N\dot{O}$	80	1.15	from τ
$(C_6H_5)_3\dot{C}$	100	0.71	from τ
 , where X = H	70	0.11	from τ
H	90	1.00	from consumption of inhibitor
Cl	80	0.14	from consumption of inhibitor
Br	80	0.17	from τ
I	80	0.36	from τ
	Pentafluorostyrene (Ref.64)		
Galvinoxyl	100	0.26	from consumption of inhibitor
Kolesch's radical	100	0.28	from consumption of inhibitor

There exist two hypotheses about the structure of the intermediate: according to one of them, it is PTHN and according to the other it is a biradical. We shall consider which hypothesis corresponds better to the thermopolymerisation inhibition data. The increase of the electronegativity of the halogen atoms in tetrahalogenobenzoquinone lowers the constant k (the reaction constant ρ is then -1).[72] On this basis, it was concluded that there exists a stage in which the halogenoquinone is subjected to the electrophilic attack by the intermediate.[72] The reactions of halogenoquinones with hydrocarbons are usually accompanied by the abstraction of hydrogen atoms. For example, 3,4,8,9-tetrahydronaphthalene, which is an analogue of PTHN, affords naphthalene on reaction with chloranil.[73] In such cases the reaction rate constant has the maximum value for quinones with the most electronegative substituents.[74] If the intermediate is PTHN, one may expect the opposite variation of the constant k on passing from chloranil to iodanil compared with that actually observed. For this reason, the occurrence of the process via a mechanism of the Diels–Alder type is ruled out.

The rate constant k for the reactions of methyl derivatives and p-benzoquinone diminishes with increase in the number of substituents and in the presence of four methyl groups cannot be measured. A similar trend has been observed in the series benzoquinone > naphthoquinone > anthraquinone.[71] This means that an unsubstituted ring carbon atom participates in the reaction of the intermediate with quinone. This conclusion has been confirmed quantitatively by the constancy of the values of k referred to a single reaction centre. An analogous deviation of the reactivity of methylquinones has been observed in reactions with methyl[75] and styryl[76] radicals; the specific constant then also remains invariant.

Since there are quantitative and qualitative analogies between the reactions of quinones with radicals and the intermediate, presumably the intermediate has a radical nature and hence should consist of a biradical. In practice it is unlikely that the rate constants for the reaction of Kolesch's radical with the intermediate would increase by 3–4 orders of magnitude on passing from H-PTHN to F-PTHN (pentafluorostyrene). It is also difficult to imagine the abstraction of a CH_3 group by diphenylpicrylhydrazyl from the PTHN formed from vinylmesitylene.[32] Finally, it has been established recently[77] that, when a nitroxy-radical is introduced at the beginning of the reaction, PTHN is not formed. On the other hand, the rate constant for its destruction in a pseudo-first order reaction with respect to Z is independent of the radical concentration. Hence PTHN is consumed unimolecularly, evidently isomerising to phenyltetralin, while the acceptor reacts with its precursor.[77] There is no doubt that this precursor can only be a biradical. Accordingly, the transfer of a hydrogen atom to the inhibitor is a result of disproportionation; the increased yield of phenyldihydronaphthalene under these conditions[66,78,79] is therefore determined by the reactions



One of the most convincing pieces of evidence for the existence of an intermediate of type PTHN is the conversion of nitroxy-radicals and DPPH radicals into hydroxylamine and hydrazine respectively.[66,78–80] However, hydroxylamine can also be formed as a result of the decomposition of its ether (recombination product).[81] On the other hand, the amount of hydroxylamine formed is only 20% of theoretical.[80] Without going into details, we may note that the change in the composition of the reaction products on treatment with DPPH, quoted by Kopecky and Hall[78] and Wiesner and Mehnert,[79] is inconsistent with the formation of an intermediate of the type of PTHN, since in this case one would expect anomalously high acceptance coefficients. Consequently the fact presented above cannot be regarded as rigorous proof of the involvement of PTHN in the reaction with stable radicals. The structure and composition of the products of the reactions of sulphur and benzoquinone are evidence against a bicyclic structure of the intermediate.[72]

Thus the structure of the products and the kinetics of the reactions of inhibitors fail to confirm, in our view, the concept of the triene structure of the intermediate and make it necessary to give preference to the hypothesis of its biradical nature.

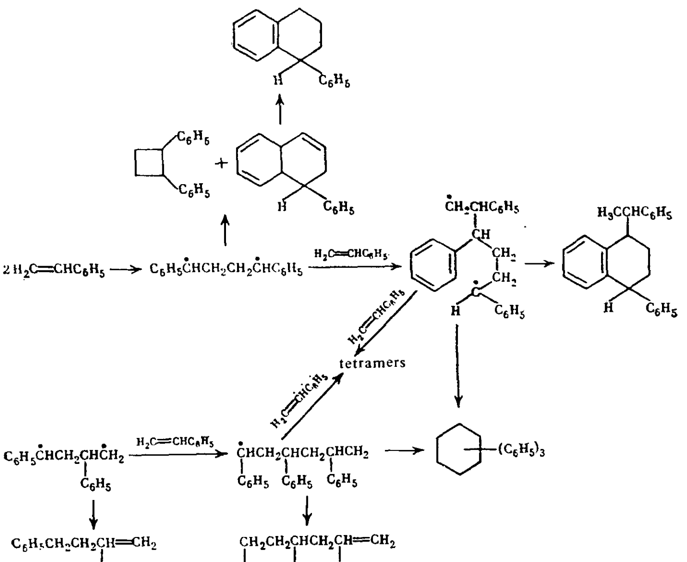
4. The Mechanism of the Thermopolymerisation of Styrene and Vinyl-aromatic Compounds

Since the main experimental data have been obtained for styrene, we shall initially analyse those concerning the mechanism of the thermopolymerisation of the above monomer.

Tetraline oligomers (PT, PPET), on the formation of which the current ideas about the thermopolymerisation mechanism are based, are not the only low-molecular-weight products of this process. Their yield is several times smaller than the overall yield of the oligomeric fraction. Together with these, linear unsaturated dimers and trimers have been identified: 1,3-diphenylbut-3-ene, 1,3,5-triphenylhex-5-ene, and triphenylcyclohexanes[11–13,82] and in the case of α-methylstyrene an unsaturated linear dimer.[46] This finding does not fit within the framework of Mayo's mechanism. In order to eliminate the contradiction, a number of workers postulated, taking into account the presence of the same olefinic compounds in the products of the thermal reaction of polystyrene, their pyrolytic formation under conditions of either chromatographic analysis[13] or direct polymerisation.[11,12]

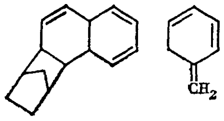
However, in the chromatography of solutions of polystyrene in ethylbenzene, subjected to preliminary heat treatment, oligomers were not detected.[72] The finding that the fraction of linear unsaturated oligomers of 1,3-diphenylbut-3-ene (DPB) and 1,3,5-triphenylhex-5-ene (TPH) decreases with increasing styrene concentration also conflicts with the above hypothesis.[12] Hence it follows that the low-molecular-weight compounds indicated are the main and not secondary thermopolymerisation products.

On the other hand, the presence of all the oligomers noted can be readily accounted for, without contradiction, within the framework of the biradical mechanism. Presumably the olifinic derivatives are formed as a result of the intramolecular disproportionation of the corresponding dimeric and trimeric biradicals, while cyclohexane derivatives are produced by their recombination and tetralin derivatives are formed via alkylation. Furthermore, the lowest biradicals can be converted into the highest by reaction with styrene molecules and then can give rise to oligomers in unimolecular reactions. This has been confirmed by the presence of tetramers among the polymerisation products[12,82] and agrees with the decrease of the fractional yield of DPB and TPH with increase in the concentration of styrene.



We shall now proceed to the discussion of the initiation mechanism. A kinetic isotope effect close to 2 has been found not only in the initiation reaction but also in the trimerisation reaction.[12] The rate of destruction of DPPH in the polymerisation of pentadeuteriostyrene is also smaller by a factor of two than in the reaction involving the non-deuteriated monomer. As already mentioned, this process is second order with respect to the monomer and its rate is limited by that of the stage involving the formation of the intermediate, which participates, according to current ideas, also in the initiation reaction. For this reason, the manifestation of isotope effects in the initiation reaction may be a consequence of their occurrence in the stage where the intermediate is formed. At the same time, on replacement of hydrogen by deuterium in the *ortho*-position, the kinetic isotope effect in the DPPH destruction process is 0.75 in the case of the thermopolymerisation reaction.[83] This indicates merely an uncertainty in the influence of the nature of the *ortho*-substituent on the formation of the intermediate, i.e. the given effect cannot be regarded as proof that the mechanism involving the generation of free radicals operates.

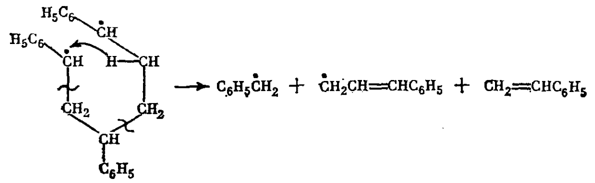
The PTHN concentration, established by UV spectroscopy, does not remain constant over several hours.[16,17] Consequently if PTHN were responsible for the formation of the initiating radicals, then the polymerisation process would not be stationary. For this reason, it is believed that[16,17] the isomer with the axial C_6H_5 group, assumed to be more reactive than the other isomers, participates in the initiation. However, as already mentioned, this intermediate should be produced via a biradical. Finally, the characteristic features of the formation of tetralin oligomers require that stationary conditions hold throughout the intermediate and not only in a fraction of the latter. It has been established[20] that close analogues of PTHN such as compounds of the type



only reduce the molecular weight of the polymer without influencing the rate of initiation. The increase of the latter has been noted only when markedly different model compounds, which can in principle themselves react with styrene to form biradicals, are used.

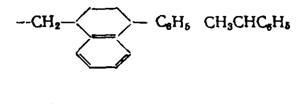
The capacity of pentafluorostyrene for thermopolymerisation cannot be explained on the basis of the structure of an intermediate of the type of PTHN. Indeed, in this case a fluorine atom should be abstracted from PTHN by a monomer molecule, which is extremely doubtful.

A possession of an initiating capacity (even though it is a weak capacity) by the biradical formed from cyclodiazo-compounds is of fundamental importance. We may note that the types of biradicals involved in the formation of monoradicals in thermopolymerisation can be various. The data of a study whose authors[84] concluded that the macromolecules have benzyl and phenylpropenyl end groups are extremely interesting in this sense. Clearly, PTHN cannot be their source. It is also unlikely that they arise in the thermal decomposition of dimers, since the rate of this reaction should be extremely low and the dimer $C_6H_5CH_2CH_2CH_2{=}CHC_6H_5$ has not been detected. Apparently the trimeric biradical



should be regarded as the source of initiating radicals.

In low-molecular-weight products of the thermopolymerisation of styrene in the presence of $FeCl_3$, the following fragments have been discovered:[85]



It has been suggested that they are due to the primary initiating radicals, which confirms Mayo's mechanism. However, they could be formed in other ways. Thus the phenyltetralin fragment can arise on chain transfer via PTHN and the phenylethyl fragment enters into the composition of the trimer.

We shall now confirm the available data on the polymerisation of styrene and other vinyl-aromatic compounds. The thermal reactions of these monomers are characterised by a series of common features: the formation of dimers having related structures (vinylthiophen, vinylfuran), the same order of the initiation reaction with respect to monomers, which is 3 (for VT, VF, 2-methyl-5-VP, and indene). It is noteworthy that also in the case of vinyl-aromatic compounds a dimeric intermediate participates in the formation of the initiating radicals. In principle, it can also be the adduct formed as a result of the Diels–Alder condensation. This possibility exists for VF, VT, VP, and β-VN, but is realisation in the case of indene, acenaphthalene, and α-VN is extremely problematical, since it requires the occurrence of fairly complex multistage rearrangements. One can therefore assume that there exists only one mechanism of the thermopolymerisation of all vinyl-aromatic monomers.

Thus the biradical mechanisms make it possible to account for the majority of experimental data, including those which do not fit within the framework of Mayo's mechanism.

Table 2. Kinetic parameters of the initiation process in the thermopolymerisation of acrylates.

Monomer	A_i, litre mol^{-1}s^{-1}	E_i, kJ mol^{-1}	t, °C	w_i, mol litre^{-1}s^{-1}	Refs.
Butyl methacrylate	—	—	80	$3\cdot10^{-13}$	[86]
Methyl acrylate	—	—	80	$5.3\cdot10^{-12}$	[86]
Methyl methacrylate	0,36	92	90	$1.7\cdot10^{-12}$	[87]
ditto	—	—	90	$1.7\cdot10^{-12}$	[86]
»	$1.1\cdot10^{-4}$	84	90	10^{-16}	[1]
»	—	—	0	$6.3\cdot10^{-13}$	[88]
Ethyl methacrylate	$10^{3.17}$	138.3	90	$1.5\cdot10^{-15}$	[89]
Methyl methacrylate	$10^{3.17}$	138.3	90	$1.5\cdot10^{-15}$	[89]
α-Chloroacrylate	$10^{6.96}$	148	80	$1.2\cdot10^{-15}$*	[89]
β-Chloroacrylate	$10^{6.3}$	158	80	$7.9\cdot10^{-16}$*	[89]

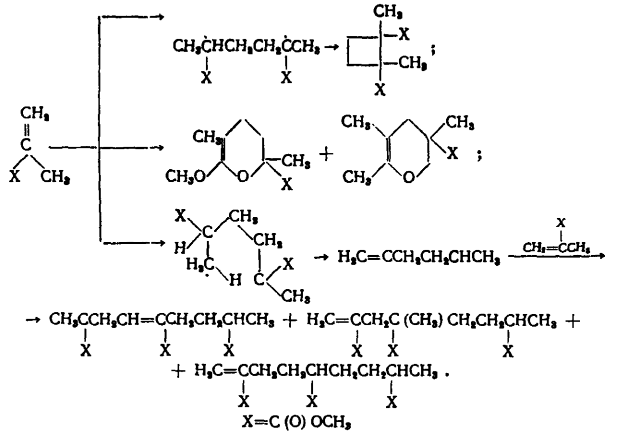
*Bimolecular initiation rate constants.

III. OXYGEN-CONTAINING MONOMERS

1. Acrylates

The kinetic data for bimolecular reactions initiating the polymerisation of acrylates in bulk, obtained in different studies or calculated by ourselves from published results, are presented in Table 2. In the analysis of the data in Table 2, the non-reproducibility of the rate of initiation of methyl methacrylate (MMA) is striking. It has been suggested[88] that this may be caused by the generation of an inhibitor in the thermal reaction. Indeed the rate of increase of viscosity for a fairly low degree of conversion diminishes as the process proceeds. Analysis shows that its reciprocal fits satisfactorily on the linear time plot. This is consistent with the hypothesis put forward by Bamford and Dewar.[88] The rate of initiation of the polymerisation of MMA at 0 °C [88] is fairly high (Table 2). According to the hypothesis of Stickler and Meyerhoff,[90] this can be caused by the accelerating effect of impurities, while pure MMA polymerises at a low rate. However, in this case one should expect a different type of time variation of the rate of increase of viscosity.

According to the data in Table 2, α-substituents (H, CH_3, C_2H_5, C_4H_9) do not exert a significant influence on w_i. An exception is Cl, whose introduction into the α-position increases the rate of initiation of polymerisation. The absolute rates of initiation quoted in a number of studies[86,87,89] differ from one another by three orders of magnitude. This can probably be explained by the causes noted above. Among the low-molecular-weight products, dimers of three types as well as linear trimers have been detected. These are formed via the following tentative mechanisms:

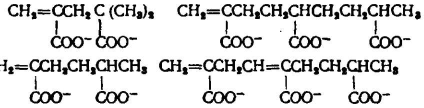


The main product is a linear dimer, the bimolecular rate constant for the formation of which is given by[91–94]

$$k\ (\text{litre mol}^{-1}\text{s}^{-1}) = 1{,}3\cdot10^{11}\exp(-107{,}2/RT).$$

Initiation is achieved as a result of the decomposition of the dimeric biradical.

In the polymerisation of methacrylic acid salts, the following products were identified in the solid phase:[95]



$CH_2{=}C(COO^-)CH_2C(COO^-)(CH_3)_2$ $CH_2{=}C(COO^-)CH_2CH_2CH(COO^-)CH_2CH_2CH(COO^-)CH_3$

$CH_2{=}C(COO^-)CH_2CH_2CH(COO^-)CH_3$ $CH_2{=}C(COO^-)CH_2CH{=}C(COO^-)CH_2CH_2CH(COO^-)CH_3$

A reaction mechanism has been proposed, in which the formation of biradicals is postulated in the first stage.[95]

The inhibition of the thermopolymerisation of acrylates by stable nitroxy-radicals—di(ethoxyphenyl)nitrogen oxide (I), the 4-hydroxy-2,2′,6,6′-tetramethylpiperidin-1-yloxy-radical (II), and the 4-benzoyl-2,2′,6,6′-tetramethylpiperidin-1-yloxy-radical—has been investigated.[86] In all cases, with the exception of methyl acrylate, the dependence of τ on $[In]_0$ is non-linear and resembles the corresponding dependence found for styrene. The results of the treatment of these data by Kurbatov's method[72] are presented in Table 3. Overall, a satisfactory agreement is observed between the rate constants calculated for different conditions. An exception is the value for the polymerisation of butyl methacrylate inhibited by compound (II). On the other hand, the values of w_i obtained using these compounds (I) and (II) agree satisfactorily. The linear dependence of τ on $[In]_0$ observed for the methyl acrylate–radical (I) pair shows that the radical is consumed in accordance with a zero-order law. The process rate constant is 6.75×10^{-9} mol litre^{-1} s^{-1}. This value exceeds almost by three orders of magnitude the rate of initiation found in experiments with the radical (III) and should therefore represent the product $nk_0[M]^2$.

The constant $k_{i,n}$ for the process involving MMA is much too high compared with that found under initiated conditions, while the value of w_i is consistent with that found by Lingnau and Meyerhoff.[89] The constants k for MMA and other monomers of this series are similar. This can be associated with the effect of strong secondary inhibition in the chain process or with the generation of an "internal" inhibitor, which reacts with alkyl radicals, as stated above. It is of interest that this feature is characteristic solely of MMA.

Table 3. The rates of initiation and the rate constants for the inhibition of the polymerisation of acrylates by nitroxy-radicals (calculated from data of Trubnikov et al.[86]).

Radical	k_{in}, litre mol^{-1}s^{-1}	k^*_{in}, litre mol^{-1}s^{-1}	w_i, mol litre^{-1}s^{-1}	10^4k, s^{-1}
		Butyl methacrylate, 80 °C		
(I)	$2.4\cdot10^6$	$5,7\cdot10^6$	$1.5\cdot10^{-11}$	2.7
(II)	$0.3\cdot10^6$	$30\cdot10^6$	$2.3\cdot10^{-11}$	0.60
		Methyl acrylate, 80 °C		
(I)	—	—	—	$\leqslant$0.1(88° C)
(III)	$4.8\cdot10^5$	$7\cdot10^5$	$3.2\cdot10^{-12}$	1.5
		Methyl methacrylate, 90 °C		
(II)	$460\cdot10^5$	$6\cdot10^5$	$4.0\cdot10^{-15}$	0.42

*The inhibition rate constants found under the conditions of initiated polymerisation.[86]

The set of data obtained in the analysis of the characteristics of the inhibition and of the composition and structure of the low-molecular-weight products shows that the thermopolymerisation of acrylate entails the formation of an intermediate, which reacts unimolecularly with the molecules of the inhibitor and the monomer. In the case considered such an intermediate can only be a dimeric biradical. By analogy with styrene, the formation of dimers in the scheme presented above can be represented as a result of its interaction with the monomer and the subsequent unimolecular disproportionation.

2. Vinyl Acetate

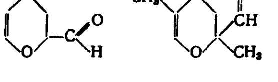
Calculated data based on the results of Starkweather and Taylor[96] have shown that the best agreement between the overall polymerisation rate constants is achieved when a kinetic order with respect to the monomer of 2.5 is adopted. One can then obtain the following expression for the rate of initiation (at 80–110 °C):

$$w_i\,(\text{mol litre}^{-1}\text{s}^{-1})=4.8\cdot10^{18}\exp(-167.2/kT)\,[M]^3.$$

It is close to that found[1] by another method. This means that the initiating radicals are formed in the thermopolymerisation of vinyl acetate with participation of monomer molecules.

3. Acrolein, Methacrolein, and Acrylic Acid

The primary products of the reaction of aldehydes are the corresponding dihydropyrans, formed as a result of 2,4-cycloaddition:[97–100]



Acrylic acid gives rise to a linear unsaturated dimer—acryloylhydracrylic acid.[99] Only the acrolein dimer is formed in the presence of hydroquinone.[99] The activation energy for the thermopolymerisation is 65.4 kJ mol^{-1}. In the presence of an amine inhibitor (whose structure and concentration have not been reported), it increases to 118.8 kJ mol^{-1}.[98] On this basis, it has been concluded that the inhibitor is active in the dimerisation stage.[98]

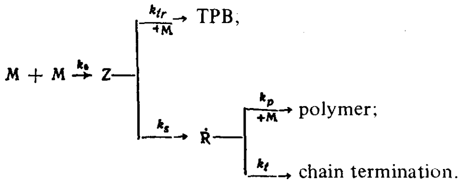
If the reaction takes place under inhibited conditions, the increment in the observed activation energy should be $0.5(E_i + E_t) - E_{in}$, where E_i, E_t, and E_{in} are the activation energies for initiation, chain termination, and the interaction of radicals with the inhibitor. For $E_{in} \cong 15$–25 kJ mol^{-1}, the quantity E_i, calculated on the basis of experiments with and without participation of the inhibitor, is 12–140 kJ mol^{-1} (the values of E_p and E_t were taken from Ham[101]), which means that the thermopolymerisation of acrolein proceeds via a radical-chain mechanism and that dimerisation is the accompanying process.

IV. MONOMERS OF THE ACETYLENE SERIES

Among the products of the thermopolymerisation of vinylacetylene, diethynylcyclobutane and the polymer which is a polyene according to the latest data[103,104] were detected.[102] The kinetic studies were performed in relation to ethynylaromatic compounds: phenylacetylene (PA), 5-ethynyl-2-methylpyridine,[105,106] and 3-ethynylphenyl phenyl ether.[107]

Apart from the polymer, 1,3,5- and 1,2,4-triphenylbenzenes (TPB),[106] whose overall yield was ~10%, were found among the products of the reaction involving PA. Since the overall rate of polymerisation is described by a kinetic equation whose order is close to two, it has been suggested that the initiators are biradicals or more precisely that one of the isomers is formed by the "tail to tail" combination of two monomer molecules, since the lowest activation energy is then expected; TPB arises as a result of the interaction of the biradicals with a monomer molecule.[106]

Analysis of the above data[106] shows that, both for PA and ethynylpyridine, the observed polymerisation rate constant, calculated subject to the condition that the reaction is of second order, is not invariant and depends on the monomer concentration. The relation $[M]^3/w = a + b[M]$, where a and b are constants, hold satisfactorily under these conditions (Fig.1). This result conflicts with the mechanism of the initiation of polymerisation by biradicals. The present author's analysis of the kinetic schemes has shown that unimolecular and bimolecular destruction of biradicals should correspond not to second order with respect to the monomer but to a higher or lower order. Hence the experimental reaction order and the dependence of the rate constant on the monomer concentration lead to the conclusion that the initiation reaction involves the formation of an intermediate Z. On this basis, one can postulate that the polymerisation mechanism is described by the following scheme:



According to this scheme, the intermediate gives rise to initiating radicals in the unimolecular reaction and to TPB in the bimolecular reaction. Chain termination takes place linearly, as has been established by Pickard and Jones.[107]

Under conditions stationary with respect to Z and $\dot{R}$, the expressions for the rate of polymerisation and trimerisation are as follows:

$$w = \frac{k_0 k_p k_s [M]^3}{k_t (k_s + k_{tr} [M])}; \tag{1}$$

$$w_{tr} = \frac{k_0 k_{tr} [M]^3}{k_s + k_{tr} [M]}. \tag{2}$$

Evidently the former agrees with the empirical relation.

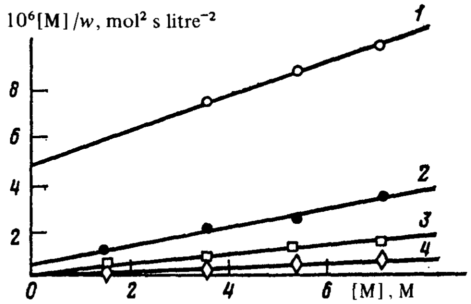


Figure 1. Dependence of the reciprocal of the measured third order rate constant for the polymerisation of phenylacetylene on its concentration at different temperatures (°C): 1) 125; 2) 140; 3) 155; 4) 170 (according to the data of Bantsyrev et al.[106]).

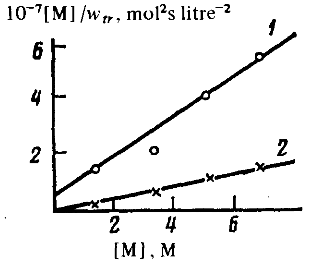


Figure 2. Dependence of the reciprocal of the third order rate constant for the formation of 1,2,4-triphenylbenzene (line 1), and 1,3,5-triphenylbenzene (line 2) at 140 °C on the phenylacetylene concentration (according to the data of Bantsyrev et al.[106]).

Treatment in terms of the second equation of data on the rate of formation of TPB isomers, which can be calculated from the results of Bantsyrev et al.,[106] confirms the validity of the proposed mechanism (Fig.2). The difference between the slopes of the linear relations in Fig.2 indicates unequal rates of generation of the precursors of the different TPB isomers. The constant k_0 is 1.5×10^{-7} litre mol^{-1} s^{-1} for 1,2,4-TPB and 5×10^{-7} litre mol^{-1} s^{-1} for 1,3,5-TPB. The straight line corresponding to 1,3,5-TPB intersects the ordinate axis near zero; consequently k_s/k_{tr} is vanishingly small. Thus the intermediate preceding 1,3,5-TPB does not participate in the initiating reaction. For 1,2,4-TPB, the above quantity, estimated from kinetic data for both polymerisation and trimerisation, is 5–6 mol litre^{-1}.

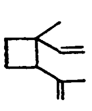
As regards the nature of the intermediate, there is no doubt that it is a biradical. Thus two types of paramagnetic species were detected by EPR in the thermopolymerisation of PA in the presence of spin trapping agents.[108] Analysis of the spectra permitted the conclusion that they arise as a result of the acceptance of the polymeric monoradical and biradical.

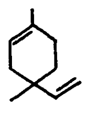
V. DIENE MONOMERS

1. Derivatives of Butadiene and Cyclic Dienes

The majority of publications concerning the thermal reactions of hydrocarbons of the divinyl series refer to the study of low-molecular-weight cyclic products formed as a result of the [2 + 4]cycloaddition. The polymerisation kinetics have been investigated only in a few early studies and to an extremely limited extent. We shall deal here with data which are of fundamental interest.

The thermal reactions of diene hydrocarbons of the divinyl series were accompanied by the formation of a polymer and dimers of three main types: derivatives of cyclobutane, vinylcyclohex-3-ene, and cyclo-octa-1,5-diene. Mainly 1-vinylcyclohex-3-ene and 4–5% of 1,2-divinylcyclobutane are formed from divinyl itself.[109] Isoprene gives rise to all the possible dimers:[110,111]


(IV)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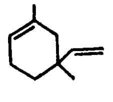
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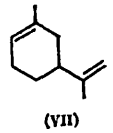
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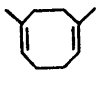
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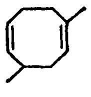

(IX)

The low-molecular-weight products of the reaction of *cis*-piperylene are only the six- and eight-membered dimers, while *trans*-piperylene gives rise to 80% of four-membered products.[111] The biisopropenyl dimer consists exclusively of dimethyl-4,6-dimenthene.[112]

The polymerisation of methylallenes leads to the formation of dimethylenecyclobutanes, which subsequently participate in secondary reactions.[113] Cyclopentadiene dimerises with an activation energy of 69 kJ mol^{-1} and the reaction is reversible.[111,114] Trimers are formed in a very small amount as a result of the cycloaddition of the monomer to the dimer.[115] Cyclohexadiene reacts via two pathways: dimerisation and polymerisation.[116]

The polymerisation reaction of all the dienes investigated is of second order with respect to the monomer. This order persists also when the reaction is carried out in dimethylformamide.[117] The results of kinetic studies are presented in Table 4. Since the overall polymerisation is a second order reaction, we may conclude that the initiation is a bimolecular process. Assuming that the activation energy for the bimolecular termination of the kinetic chains E_t is close to 8 kJ mol^{-1}, while $A_t = 10^7 - 10^8$ litre mol^{-1} s^{-1} as for the majority of monomers, we obtain $E_i \cong 92$ kJ mol^{-1} and $A_i \cong 8$ to 80 litre mol^{-1} s^{-1} for isoprene, while the corresponding values for biisopropenyl are 88 kJ mol^{-1} and 0.1–1 litre mol^{-1} s^{-1} respectively. The constants k_p were taken from Kauffmann et al.[16] (p.120) and Starinchikova and Svetlov[127] (p.342). Since the pre-exponential factors A_i found are fairly low, one can assume that the initiation rate constant is an effective quantity. This is possible only when the radicals are formed via an intermediate Z, which is also converted competitively, for example, into dimers. The reaction mechanism can be formally represented schematically as follows:

$$\begin{tikzcd} & & \dot{R}\,; \\ M + M \arrow[r, "k_0"] & Z \arrow[ur, "k_s"] \arrow[dr, "k_d"'] & \\ & & D. \end{tikzcd}$$

According to this scheme, the rate of initiation is defined by the expression

$$w_i = k_0 k_s [M]^2/(k_s + k_d).$$

Then, assuming that $k_s \ll k_d$ and adopting $E_d \cong 84-92$ kJ mol^{-1} and $A_d \cong 10^6-10^7$ litre mol^{-1} s^{-1}, we obtain $E_s - E_d \cong 0$ and $A_s/A_d \cong 10^{-6}-10^{-4}$. It is noteworthy that no measurements were made of the initiation reaction order on the basis of concentration; one cannot rule out that it amounts to 2.5 and that the rate constant k_s actually characterises a bimolecular process.

Table 4. Kinetic parameters of the reactions involving the formation of polymers (P) and dimers (D) from diene monomers.

Monomer	Reaction product	E, kJ mol^{-1}	A, litre mol^{-1}s^{-1}	Refs.
Isoprene	(VII)	94	$1.8 \cdot 10^7$	[118]
»	(V) + (VI) *	90	$1.4 \cdot 10^6$	[118]
»	D	104	$7.9 \cdot 10^7$	[119]
»	P	78,6	$3.4 \cdot 10^7$	[118]
Biisopropenyl	D	92	$2.1 \cdot 10^6$	[118]
»	P	73	$2.2 \cdot 10^3$	[118]
cis-Piperylene	D	93	$2.1 \cdot 10^5$	[111]
trans-Piperylene	D	81,5	$8.7 \cdot 10^4$	[111]
Cyclopentadiene	D	62	$4.0 \cdot 10^5$	[111]
1,2-Dimethylallene	D	116	$3.4 \cdot 10^7$	[113]
Cyclohexa-1,3-diene	D	86	$4 \cdot 10^4$	[116]
»	P	96,5	$1.7 \cdot 10^5$	[116]

*Gapon[118] called this product the second dimer, while according to Nazarov et al.[110] it is a mixture of compounds (V) and (VI).

In our view the intermediate is none other than a biradical. The formation of biradicals in the thermopolymerisation of dienes has been confirmed by the presence of four-membered cyclic dimers. It has been established[119] that the volume of the transition state in the dimerisation of isoprene is greater by 21–23 cm^3 mol^{-1} than the volume of the dimer. On passing from six-membered rings to the corresponding linear hydrocarbons, the same increase in specific volume occurs. On this basis, it has been concluded that the intermediate is indeed a biradical. The dimerisation of 1,4-dideuteriobutadiene is accompanied by a decrease of the stereospecificity of the dienophile component by 10%.[121]

2. Chloroprene

The thermopolymerisation of chloroprene is accompanied by the formation of products of the same type as for other 1,3-dienes, namely compounds corresponding to divinylcyclobutane (X),[122] two vinylcyclohexene (XI) isomers, and cyclooctadiene.[123] The first two products predominate at high temperatures (95 °C) and the compound of type (X) isomerises to (XI). The polymer is linear *cis*-polychloroprene.[124] The dimers and the polymer are formed in accordance with a second-order law at different rates and with different activation energies; the latter differ little for the 4- and 6-membered isomers, amounting to 84–86 kJ mol^{-1}.[124,125] Typical inhibitors suppress the formation of the polymer but do not affect dimerisation,[124] DPPH being converted under these conditions into the corresponding hydrazine.

However, a number of significant differences make it necessary to regard the mechanism of the thermopolymerisation of chloroprene as extremely stereospecific and different from the mechanism of the reactions of other dienes. At the end of the induction period, associated with the exhaustion of the inhibitor, the concentration of the dimer falls, tending to ~1 wt.%, while the polymer is formed at a constant rate.[125] If the reaction is carried out without an inhibitor, then the concentration of dimers increases from a certain initial value to a limiting value, which is also close to 1 wt.%. These findings enabled the authors[124] to reach the unusual conclusion that the polymer is formed exclusively from the dimer; there is no doubt about its validity.

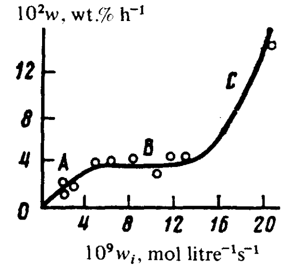


Figure 3. Dependence of the rate of polymerisation of chloroprene on the rate of initiation at 35 °C.[125]

The method used in the preliminary treatment of the monomer, especially, the degree of elimination of oxygen from the latter and the degree of its reduction, exerts the main influence on the rate of polymerisation. Chloroprene dimers do not polymerise, but the introduction of the monomer renders this process possible. The authors[125] suggested that the polymerisation initiator is an oxidised form of the monomer, which is not determined as the peroxide. The relation between the rates of polymerisation and initiation of chloroprene (the latter was estimated from the consumption of DPPH) is characterised by the presence of different sections *A*, *B*, and C (Fig.3) whose existence has been explained as follows.[125] After the careful removal of oxygen, the concentration of catalytic species Y is small and the rate of polymerisation is lower than that of dimerisation. Indeed, along section *A*, the sum of the concentrations of the dimers and the polymer is approximately equal to the concentration of the dimers formed in the presence of the inhibitor. Along section *B*, the rate of polymerisation is constant and equal to the rate of dimerisation in the presence of the inhibitor regardless of the rate of initiation. This means that [Y] is large and the rate of conversion of the dimers into the polymer is much higher than the rate of their formation. In order to explain section C of the curve, the monomer brought into contact with oxygen was employed and there is no doubt that the increase in the rate of polymerisation in this region is associated with the influence of a polyperoxide.[126]

Taking into account all the facts described, one may conclude that the monomer contains catalytic species which lead to the polymerisation of the dimers via ring opening. In the presence of inhibitors, these species are not destroyed. Therefore, there should exist an active centre (I), originating from the catalytic compound Y. It participates in the kinetic chain propagation and termination reactions and in the latter case the catalyst Y is regenerated.

We believe that the following mechanism is most probable:

$$\mathrm{M}+\mathrm{M}\xrightarrow{k_0}\mathrm{D};\qquad \mathrm{D}+\mathrm{Y}\xrightarrow{k_s}\mathrm{I};\quad \mathrm{D}+\mathrm{I}\xrightarrow{k_p}\mathrm{P};\quad \mathrm{I}\xrightarrow{k_t}\text{chain termination.}$$

The steady concentration of dimers can be found from the equation which follows from the above scheme:

$$0.5\left(\frac{k_t}{k_0k_pk_s[\mathrm{Y}][\mathrm{M}]^2}\right)^{0.5}\ln\frac{([\mathrm{D}]_{st}+[\mathrm{D}])([\mathrm{D}]_{st}-[\mathrm{D}]_0)}{([\mathrm{D}]_{st}-[\mathrm{D}])([\mathrm{D}]_{st}+[\mathrm{D}]_0)}=t, \qquad (3)$$

where $[\mathrm{D}]_{st}$ is the stationary concentration of the dimer.

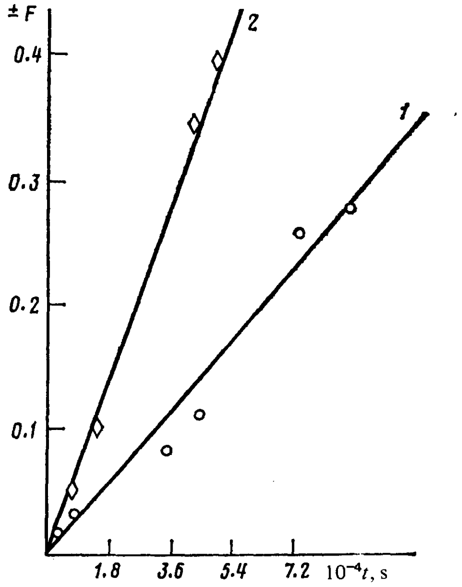


Figure 4. Semilogarithmic representation of the kinetics of the attainment of a stationary chloroprene concentration (at 35 °C): 1) calculation based on the accumulation of the dimer; 2) calculated based on the consumption of the dimer (according to the data of Billingham et al.[125]).

Calculation of the change in the concentration of the dimers by this equation both in experiments with the inhibitor and without it makes it possible to obtain the linear relations presented in Fig.4. In the second case, the sign of the function

$$F=\ln\frac{([\mathrm{D}]_{st}+[\mathrm{D}])([\mathrm{D}]_{st}-[\mathrm{D}]_0)}{([\mathrm{D}]_{st}-[\mathrm{D}])([\mathrm{D}]_{st}+[\mathrm{D}]_0)}$$

is negative. Since it is impossible to determine $[\mathrm{D}]_{st}$ accurately from the data presented, we assumed that it is approximately 1%. If it is ~1.5%, then the sign of F becomes positive. Evidently the authors[125] used monomer specimens with different concentrations [Y], which determine $[\mathrm{D}]_{st}$. The validity of the formal relations, which also show that $[\mathrm{I}] \ll [\mathrm{Y}]$, is of fundamental importance.

Within the framework of the scheme presented above, the rate of polymerisation is described by the expression

$$w=\frac{k_pk_s}{k_t}[\mathrm{Y}][\mathrm{D}]^2. \qquad (4)$$

After substituting in Eqn.(4) the expression for the steady concentration of the dimers, we obtain

$$w=\frac{k_pk_s}{k_t}[\mathrm{Y}][\mathrm{D}]_{st}\left(\frac{\beta e^{-\alpha t}-1}{\beta e^{\alpha t}+1}\right),$$

where

$$\alpha=2\left(\frac{k_0k_pk_s[\mathrm{Y}][\mathrm{M}]^2}{k_t}\right)^{0.5};\quad \beta=\frac{[\mathrm{D}]_{st}+[\mathrm{D}]_0}{[\mathrm{D}]_{st}-[\mathrm{D}]_0}.$$

Since

$$[\mathrm{D}]_{st}=\left(\frac{k_0k_t[\mathrm{M}]^2}{k_pk_s[\mathrm{Y}]}\right),$$

it follows that, for large values of [Y], $w = k_0[\mathrm{M}]^2$.

Two questions are of decisive important for the mechanism of the thermopolymerisation of chloroprene: (a) the nature of the catalytic species and of the active centre; (b) the mechanism of the ring opening. It is as yet difficult to give a definite answer to these questions.

On the grounds that substances tending to undergo homolytic reactions exhibit an inhibiting activity, presumably I is a radical in nature and diphenylpicrylhydrazine is formed as a result of a disproportionation reaction. Then the interaction of the dimer and Y should result in the formation of an extremely specific radical, which reacts with the dimer but not with the monomer. The equality of the rates of dimerisation and polymerisation suggests either the involvement of the dimers of all types in the second process or the establishment of equilibrium between them via the intermediate. There exists also the view that the rearrangement proceeds via the formation of a biradical.[121] This may explain the observed characteristics of the polymerisation, although the mechanism of the stabilisation of the biradicals by the catalytic species is obscure.

3. Divinyl Sulphide

The elementary units of the polymer macromolecules formed from divinyl sulphide have the thiophane structure.[127] The order of the overall polymerisation reaction with respect to the monomer is 2.1 and the activation energy is 50.2 kJ mol^{-1}. The activation energy for thermal initiation (62 kJ mol^{-1}) and the pre-exponential factor for the rate constant (~10^3 litre mol^{-1} s^{-1}) can be estimated from the data of Starinchikova and Svetlov.[127]

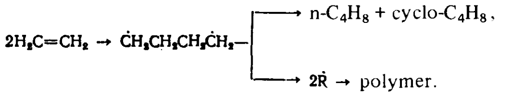
VI. ETHYLENE

The thermal reactions of ethylene have been investigated in the gas and liquid phases. At temperatures below 400 °C, polymerisation mainly takes place[128] (p.125). The primary reaction products detected consisted of 31.7% of butenes, 12.6% of cyclobutanes, and also propene and higher olefins. The activation energy for the formation of lower hydrocarbons is 475 kJ mol^{-1}. The kinetic order of the polymerisation reaction with respect to ethylene at sufficiently high conversions is close to two but at early stages it amounts to 2.3 to 2.5.[129]

The polymerisation of ethylene in solution in naphthalene is characterised by a kinetic order of 2.6, an activation energy of 170 kJ mol^{-1}, and a pre-exponential factor of $10^{10.1}$ litre mol^{-1} s^{-1}.[129] It has been suggested[129] that the reaction order observed is determined by the stage involving the formation of the intermediate. It is believed[128] that the initiating radicals arise when a hydrogen atom is transferred from one ethylene molecule to another. The observed activation energy for the initiation stage is consistent with this hypothesis but one cannot rule out the possibility of the formation of the tetramethylene biradical as the intermediate.[128]

The data of Russell and Hottel[129] permit the conclusion that the order of the initiation reaction with respect to ethylene is 3. When w_i (mol litre^{-1} s^{-1}) = $10^{15}\exp(-272/RT)\,[\mathrm{M}]^3$.

Bearing in mind that the reaction considered is of third order and also taking into account the formation of cyclobutane and butene, its mechanism can be represented by the following scheme involving the tetramethylene biradical:



$$2H_2C{=}CH_2 \rightarrow \dot{C}H_2CH_2CH_2\dot{C}H_2 - \begin{cases} \rightarrow n\text{-}C_4H_8 + \text{cyclo-}C_4H_8, \\ \rightarrow 2\dot{R} \rightarrow \text{polymer.} \end{cases}$$

Chlorotrifluoroethylene and tetrafluoroethylene give rise to only the corresponding cyclobutane derivatives.[130]

VII. CONCLUSION

Analysis of the results of the study of the thermopolymerisation of monomers of different classes permits certain general conclusions concerning the mechanism of this reaction.

The low-molecular-weight products of the given process can be various but as a rule they are dimers. Phenylacetylene gives rise to the trimer only. Mixtures of different dimers and trimers are produced from styrene and MMA and tetramers have also been detected.

The polymerisation of all monomers, with the exception of chloroprene, proceeds in accordance with the classical radical-chain mechanism. The initiating radicals are generated via an intermediate which is in most cases a biradical. Although the formation of PTHN as an intermediate has in fact been postulated for styrene, a number of results conflict with this hypothesis. There is probably no point in assuming a special exceptional mechanism for this monomer, which does not exhibit any anomalous properties. The third order of the initiation stage with respect to the monomer shows that the radicals are formed as a result of the interaction of the dimeric biradical with the monomer, which subsequently decomposes, producing, for example, in the case of styrene, the benzyl and phenylpropenyl radicals. Judging from the fairly low pre-exponential factors in the expressions for the initiation rate constants, the third kinetic order is to be expected for MMA, isoprene, bi-isopropenyl, indene, and divinyl sulphate. The primary radical is then preferentially converted into the dimer, which is confirmed in many instances either by the absence of trimers or by their low yield. On the other hand, when the competing reaction of the biradical with the monomer takes place to an appreciable extent, the reaction order may become less than three, falling to two. In order to establish the true reaction order, detailed kinetic studies are required and these have been by no means always carried out. In contrast to other monomers, in the polymerisation of phenylacetylene monoradicals arise in the decomposition of a dimeric biradical, whose reaction with the monomer leads to the formation of triphenylbenzene. The initiating radicals are not formed at all or are formed with a low yield in the thermopolymerisation of trifluorostyrene and acrylonitrile[101] (p.221), whose only products are the corresponding four-membered dimers.[131] A similar situation has been observed for α- and β-halogenostyrenes.

It is noteworthy that, when the classical values of the pre-exponential factors are used for the rate constants for the elementary stages involved in the initiation process, it is impossible to account for the high pre-exponential factors in the expression for the initiation rate constants for monomers such as ethylene and vinyl acetate, which amount to ~10^{15} and 10^{18} litre^2 mol^{-2} s^{-1} respectively. On the other hand, this can be explained by the fairly low values of A for the stages where the biradicals are converted into low-molecular-weight compounds or for their reversible decomposition with formation of the monomer and, on the other, by the more complex expression for the overall rate constant, which is determined by the characteristic features of the mechanism.

In contrast to other methods of generating similar reactive species, such as the decomposition of cyclic diazo-compounds or the thermolysis of cyclobutanes, in the thermal reaction of the monomers there is a possibility of the formation of biradicals with different configurations. It has been noted correctly[121] that the "uncoiled" forms of biradicals are less susceptible to unimolecular recombination, since for the occurrence of the latter it is essential that the biradical should assume a cyclic form, from which the cyclic dimer can be readily produced. Indeed, inhibitors do not influence the formation of diphenylcyclobutane in the decomposition of tetrahydropyridazines and in the thermal reaction of styrene.[19] The rate of generation of the initiating monoradicals is also extremely low. Biradicals in an acyclic conformation are capable of reacting unimolecularly also via disproportionation and alkylation. There is also a possibility of a bimolecular reaction, for example, the reaction with the monomer. Judging from data of Kirchner and Burhholz,[12] the ratio k_d/k_{tr} for styrene should be 2.3. Since the deviation from the zero order of the DPPH destruction reaction occurs at the concentration (DPPH) ≅ 10^{-5} M,[63] it follows that $k_b/k_{tr} \cong 8.7 \times 10^5$.

The rate constants for the destruction of biradicals generated in the photochemical reactions of ketones (Norrish type 2 reactions) in the presence of various acceptors (oxygen, bipyridyl hydrochloride, dibutyl selenoketone) are (4–6) × 10^9 mol^{-1} s^{-1},[132,133] i.e. exceed significantly in absolute magnitude the constants known for monoradicals. A similar phenomenon had been observed earlier for nitroxy-biradicals.[134] In order to account for this finding, the concept of the adiabatic nature of the reactions was resorted to[134] (pp.378, 386). If it is assumed that the rate constants for the reactions of the dimeric styrene biradicals with DPPH are also diffusion dependent, it is possible to calculate $k_{tr} \cong 5 \times 10^3$ litre mol^{-1} s^{-1} and $k_d \cong 10^4$ s^{-1}. The latter quantity may be too low, but even in the case of cyclic biradicals, whose conversion into a state favourable for recombination requires virtually no rotation about the C–C bonds, there exists a competing reaction with divinyl.[135]

The question whether the initiating radicals and all the low-molecular-weight compounds are formed via the same intermediate is of fundamental importance. There is perhaps no doubt that this is true (a) for styrene, because it is supported by evidence obtained in the study of the thermopolymerisation kinetics, the structures of the compounds produced, and the influence of radical acceptors and (b) for monomers whose thermopolymerisation gives rise preferentially to oligomers with a linear structure, which are formed via an intermediate (methacrylates).

However, for the monomers giving rise to low-molecular-weight 2,4-cycloaddition products, the answer to the question posed above is not unambiguous. The possibility of the formation of small amounts of four-membered or linear dimers cannot be ruled out even in those cases where the main product is a six-membered compound (2,3-dimethylbutadiene). On the other hand, there exists the hypothesis that 2,4-cycloaddition reactions take place via two competing mechanisms: synchronous and biradical.[136] The second pathway may be responsible for the initiation of the polymerisation. According to most investigators, the activation energy for the biradical process should be significantly higher than for the synchronous process[121] and its contribution should be correspondingly lower.

Thus in the given case the problem also reduces to the familiar problem of the mechanism of pericyclic reactions. Having analysed numerous facts, Firestone[121] concluded that the biradical mechanism makes it possible to explain virtually all the experimental data, while the synchronous mechanism is inconsistent with many of them.

Overall, one may conclude that there exists a general mechanism of the thermal reactions of many monomers. Specific differences may be observed for individual representatives of substances of this kind.

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The Electronic Structure of Superhalogens and Superalkalies

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Molecular systems with anomalous values of the first ionisation ptoentials or electron affinity have been examined. On the basis of the results of calculations by the DV-X_α method it has been possible to relate the values of the electron affinity and the first ionisation potential to the characteristic features of the electronic structure of these compounds. The analysis carried out has made it possible to distinguish two large classes of chemical compound: with an anomalously high electron affinity (superhalogens) and with anomalously low first ionisation potentials (superalkalies). Estimates of the maximum possible electron affinity of chemical compounds have been given, and ways of finding these systems have been outlined. Various possible manifestations of high electron affinity and low first ionisation potentials in the physicochemical properties of superhalogens and superalkalies have been examined.
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I. INTRODUCTION

Molecular systems exhibiting extremal characteristics are of particular interest from both theoretical and practical viewpoints. The theoretical study of these systems facilitates the appearance of new fundamental ideas on the physicochemical properties of matter, and the use of these systems in technology extends considerably the range of constructional materials.

The electron affinity (EA) and the first ionisation potential (IP) are the most important characteristics of molecules, so that molecules exhibiting the maximum values of the EA or the minimum values of the IP are of particular interest for chemistry. Systems with high EA play an important role in the synthesis of compounds of new classes. For example, the synthesis of the compound $Xe^+[PtF_6]^-$,[1,2] with which the chemistry of the noble gases began, was carried out using platinum hexafluoride PtF_6, which has a high EA. Subsequently, systems with high EA have been used to synthesise many new compounds, such as $XeF^+[RuF_6]^-$, $XeF_5^+[RuF_6]^-$,[3] $Xe_2F_3^+[AsF_6]^-$,[4] $KrF^+[SbF_6]^-$,[5] and many others,[6-12] and also compounds containing clusters of non-transition elements of the type Te_4^{2+}, Bi_5^{3+}, and S_8^{2+} as cations.[13]

Systems with high EA have recently been used as a basis for the synthesis of organic superconductors,[14-20] and also to modify the electronic structure of conjugated polymers (polymer doping) [21-25] and graphite (intercalation of graphite).[26] Systems with low first IP are also important for preparing new compounds, and the first salts of this type, $Li_3O^+[NO]^-$ and $Li_3O^+[NO_2]^-$ have already been synthesised.[27-29]

The anomalous EA and IP values are apparently related to the characteristic features of the electronic structure of the chemical compounds, so that it is of undoubted interest to study the electronic structure of molecular systems exhibiting anomalously high EA values and anomalously low IP values. This problem is dealt with in the present review.

II. ELECTRON AFFINITY

The electron affinity of a molecule or radical is defined as the decrease in the energy of the system when one electron is added. For molecules it is possible to distinguish two types of EA: adiabatic and vertical. The adiabatic EA of a neutral molecule is the difference between the total energies of the neutral system for its equilibrium geometry (R_e) and the negatively charged system, again for the equilibrium geometry (R_e^-):

$$\mathrm{EA}_{\mathrm{ad}} = E(R_e) - E^-(R_e^-) \qquad (1)$$

The vertical EA is the difference between the total energies of the neutral and charged systems for the equilibrium geometry of the neutral system (R_e):

$$\mathrm{EA}_{\mathrm{vert}} = E(R_e) - E^-(R_e) \qquad (2)$$

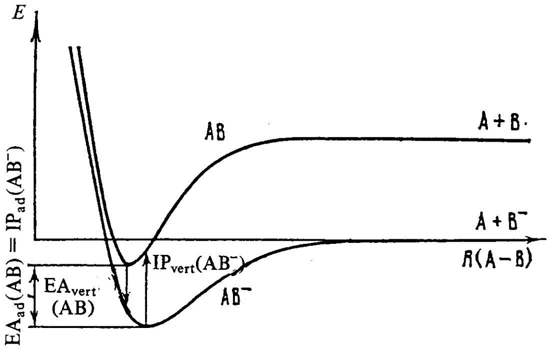

Figure 1. Diagram illustrating the definition of adiabatic and vertical EA and IP for the case of a diatomic molecule AB (R is the distance between the atoms A and B).

Moreover, for a negatively charged system it is possible to define the upper ionisation potential (IP), which also may be vertical and adiabatic. The adiabatic IP of a negative ion is equal to the difference between the total energies of the neutral system for its equilibrium geometry and the negatively charged ion for its equilibrium geometry:

$$\mathrm{IP}_{\mathrm{ad}} = -[E^-(R_e^-) - E(R_e)] \qquad (3)$$

Eqn.(3) shows that the adiabatic IP of a negative ion coincides exactly with the adiabatic EA of the neutral molecule. The vertical IP is equal to the difference between the total energies of the charged system and the neutral system for the equilibrium geometry of the ion:

$$\mathrm{IP}_{\mathrm{vert}} = -[E^-(R_e^-) - E(R_e^-)] \qquad (4)$$

The vertical IP of a negative ion differs from the vertical EA of the neutral system. The difference between the vertical and adiabatic values of the EA and IP is called the adiabatic correction.

$$\begin{aligned}\mathrm{EA}_{\mathrm{ad}} &= \mathrm{EA}_{\mathrm{vert}} + \Delta\mathrm{EA}_{\mathrm{ad}}\\ \mathrm{IP}_{\mathrm{ad}} &= \mathrm{IP}_{\mathrm{vert}} + \Delta\mathrm{IP}_{\mathrm{ad}}\end{aligned} \qquad (5)$$

These definitions of the EA and IP are illustrated graphically in Fig.1.

It should be emphasised that in practice, all three experimental values of $\mathrm{EA}_{\mathrm{ad}}$, $\mathrm{EA}_{\mathrm{vert}}$, and $\mathrm{IP}_{\mathrm{vert}}$ are not known simultaneously for any system. The values are equal to within the adiabatic corrections, however, so that is is necessary to consider in more detail the estimation of the values of these corrections. An analysis of the experimental photoelectron spectra of the molecules SF_6, C_6H_6, MoF_6, WF_6, and UF_6[30] showed that $\Delta\mathrm{IP}_{\mathrm{ad}}$ is generally small (usually 0.1–0.2 eV) and does not exceed 0.5 eV. The experimental photoelectron spectra of BrF_5 and IF_5[31] also indicate that the difference between $\mathrm{IP}_{\mathrm{ad}}$ and $\mathrm{IP}_{\mathrm{vert}}$ is small (0.4–0.6 eV).

The low values of the adiabatic corrections for these molecules are related to the fact that the electron is removed from non-bonding molecular orbitals (MO). Approximately the same $\Delta\mathrm{EA}_{\mathrm{ad}}$ values should be expected in those cases where the additional electron occupies a non-bonding MO. In those cases where the electron enters an antibonding MO, however, the value of the adiabatic correction may reach 1.5–3 eV. According to non-empirical calculations of the electronic structure of the SF_6 molecule and the SF_6^- anion, allowance for geometric relaxation in the bond lengths of the SF_6 molecule leads to an increase in the EA by 2.5 eV.[32] Calculations of the EA of the molecules PF_5, AsF_5, and SbF_5 by the present authors show that for these molecules, $\Delta\mathrm{EA}_{\mathrm{ad}} \cong 2.8$ eV, and that the negative ion has a square pyramidal structure, whereas the neutral molecule has a trigonal bipyramidal structure.

Thus in the case where the additional electron occupies a non-bonding MO, the adiabatic correction is small (~0.5 eV). If the treatment is restricted to an error of 0.5 eV (this can be done in those cases where the EA value is small), then to determine the EA it is sufficient to know one of the quantities $\mathrm{EA}_{\mathrm{ad}}$, $\mathrm{EA}_{\mathrm{vert}}$, or $\mathrm{IP}_{\mathrm{vert}}$. In this approximation, the problem of calculating the EA is simplified considerably, since it is possible to replace the geometry of the radicals, which is often unknown, by the geometry of negative ions with closed shells, which is known from crystallographic data for corresponding salts.

Thus for systems of the type being discussed, it is possible to distinguish two levels of the study of EA. The first level corresponds to a crude estimate of the EA, when the difference between the values of $\mathrm{EA}_{\mathrm{ad}}$, $\mathrm{EA}_{\mathrm{vert}}$, and $\mathrm{IP}_{\mathrm{vert}}$ is neglected. At this level, the errors in the estimation of the EA may reach 0.5–1.0 eV. At the second level, it is necessary to take account of $\Delta\mathrm{EA}_{\mathrm{ad}}$ and $\Delta\mathrm{IP}_{\mathrm{ad}}$, and in the comparison with the experimentally determined values it is necessary to take account of the conditions under which the experiment was carried out. At the second level, the errors should not exceed 0.1–0.2 eV. At present, it is apparently possible to reach the second level of the determination of electron affinity for small radicals, but for most systems, existing theoretical methods make it necessary to restrict the treatment to the first level.

When the additional electron occupies an antibonding MO, all three quantities ($\mathrm{EA}_{\mathrm{ad}}$, $\mathrm{EA}_{\mathrm{vert}}$, and $\mathrm{IP}_{\mathrm{vert}}$) may differ considerably, and they must be examined separately.

A large number of methods are used for the experimental determination of the EA: photo-ionisation,[33,34] surface ionisation,[35,36] fragmentation by electron impact,[34] molecular photodissociation,[34] equilibrium sublimation,[37] radiative addition of an electron,[37] measurement of crystal lattice energies,[37] charge-transfer reactions,[38,39] photosensitive ionisation,[34] and others.[40,41] The greatest experimental success[34,40] has been achieved by the laser photo-ionisation of negatively charged systems, but it is applicable only to substances which can be obtained in the gas phase in a sufficient concentration. In spite of the wide range of experimental methods, the results of the determination of the EA in early studies often do not agree with one another. For example, for the NO_2 radical the experimentally determined EA values lie in the range 1.6–4.0 eV; according to some authors, $EA(NO_2) > 3.613$ eV, and according to others, $EA(NO_2) < 3.063$ eV.[38,39]

An alternative method of estimating EA is provided by quantum-chemical calculations. One of the most important aims of both experimental and theoretical studies of EA is undoubtedly the search for simple models which would make it possible to predict qualitatively whether an EA has a high or a low value. The study of systems having anomalously high EA is of particular interest.

The direct calculation of EA is a difficult problem in quantum chemistry. The use of Koopmans' theorem[42] or the ΔSCF procedure[43] to estimate EA gives values which often differ from the experimental values by 2–3 eV.[44] The use of non-empirical methods with allowance for correlation[44–49] makes it possible to calculate EA with an accuracy of 0.1 to 0.2 eV, but their application at present is restricted to small molecules.

X_α methods, which make it possible to examine comparatively large systems, have recently begun to be used for EA calculations.[44]

Calculations of the electronic structure of a large number of molecules by X_α methods show that these methods are very effective for large systems and practically always ensure the correct order of magnitude of the calculated IP values with comparatively small deviations from the experimental IP values. The X_α calculation procedure has been described in sufficient detail,[44,50–55] and will not be described in the present work.

Among the elements of the periodic system, halogen atoms have the highest EA (3.0–3.6 eV). In molecules and polyatomic radicals, as a result of collective effects, the EA may be higher than the EA of the halogens. These systems are called superhalogens.

III. ELECTRONIC STRUCTURE OF SUPERHALOGENS

In the examination of systems with anomalously high EA values, two problems arise. Firstly, it is necessary to outline the range of molecules which can be regarded as superhalogens. Secondly, it is necessary to determine the highest EA values that molecular systems in general can have, and also the specific cases in which maximum EA values can be expected.

Simple qualitative ideas relating the EA value to the characteristics of the electronic structures of chemical compounds have been formulated.[56–58] These ideas make it possible to distinguish a class of compound with high EA; the arguments on which they are based will be discussed in detail below.

For the development of models it is natural to use the orbital approach, which is widely employed to interpret electronic, photoelectron, and X-ray electron spectra, and which also forms the basis of the Woodward–Hoffman rules, according to which the energies of the MO formed by AO of the same type should lie in the following order: ε(bonding) > ε(non-bonding) > ε(antibonding). Thus the value of the EA can be related to the structure of the lowest unoccupied MO (LUMO) of the neutral system, which generally accepts the additional electron on formation of an anion, and the value of the first IP of the anion can be related to the structure of its highest occupied MO (HOMO). This gives the corresponding order: IP(bonding) > IP(non-bonding) > IP(antibonding), that is the EA value depends on the type of HOMO of the anion.

A second important factor influencing the magnitude of the EA of a molecule is the value of the EA of the atoms making up the molecule. The higher the EA of the atoms, the higher may be the EA of the compound as a whole. It is therefore possible to have cases where, in spite of the antibonding character of the HOMO of the anion, and as a result of the high EA of the atoms making up the molecule, the EA of the whole molecule will be greater than that of a molecule for which the HOMO of the anion is non-bonding or even antibonding, but in which the values of the EA of the individual atoms are low.

A third important factor influencing the value of the EA of a molecule is the degree of delocalisation of the "additional" electron. According to traditional ideas,[59] the smaller the fraction of an electron $\delta\bar{e}$, added to an atom, the easier it is for the atom to retain it. In the limiting case, when $\delta\bar{e} \to 0$, the IP of the anion approaches the IP of the neutral molecule, which is fairly high. Thus the EA should increase with increase in the extent of the delocalisation of the electron over an increasing number of electronegative atoms making up the molecule.

Calculations by the present authors for the model system $F + \delta\bar{e}$, where $\delta\bar{e} = 0.1, 0.2, \ldots 1.0$ show that the ratio $[E(F + \delta\bar{e}) - E(F^-)]/\delta\bar{e}$, where E is the total energy, increases with decrease in $\delta\bar{e}$. The greatest contribution to the difference in the energies is made by the energies of attraction to the nucleus and interelectron repulsion, and the contributions from the kinetic and exchange energies are small. The electron affinity of the F atom is determined by the energy of the HOMO of the anion, which in turn is determined by the overall potential. Increase in $\delta\bar{e}$ is accompanied by an increase in the shielding of the nucleus, that is the effective charge of the nucleus decreases, leading to a decrease in the energy of the level determining the EA.

In addition to these basic factors, the value of the EA is also influenced by various other specific factors, which will be discussed below. The above three factors are sufficient, however, to formulate the conditions which must be satisfied by systems with anomalous EA or IP values. These limiting cases and the possible consequences of anomalous IP and EA values for chemistry will be discussed in detail below.

The ideas presented above can be applied first to molecules and radicals of the type MX_k. For the EA of these systems to be high, it is necessary that the ligands X be electronegative atoms with high EA, for example halogen or oxygen atoms. Moreover, it is desirable that the HOMO of the corresponding anion be bonding. If however the ligands are halogen or oxygen atoms (and in general if the ligand atoms have many electrons), the HOMO of the compounds are either non-bonding or antibonding. When the HOMO is non-bonding, the EA of the compound MX_k will be greater than the EA of the ligand atoms X as a consequence of the high EA of the atoms and the effect of charge delocalisation.

It should be noted that in those cases where the HOMO, from its symmetry, is antibonding, but the actual contribution of the central M to this orbital is very small (that is, it is essentially non-bonding), high EA can be expected for MX_k. An additional reason for the appearance of high EA values is observed in compounds MX_k where the ligands X are halogen or oxygen atoms and the central atom M has a positive charge which ensures additional stabilisation of the electron delocalised over the ligands. Calculations carried out[56] for a system consisting of an F^- ion with a point positive charge, separated from the F^- nucleus by 3.0 a.u., showed that increase in the point charge by +0.1 e increases the EA of the F atom by ~1 eV. Thus the greater the charge on the M atom, the greater may be the EA.

The above ideas on the relationship between the magnitude of the EA and the electronic structure of a compound can be presented in the language of localised MO. If in an ion MX_k^- with electronegative ligands the central atom does not have lone pairs of electrons (LPE), while the radical MX_k does not contain unpaired electrons localised on the M atom, and all the valence electrons are distributed among the localised MO of the bonds and the LPE of the ligands X, the additional electron will be delocalised over the electronegative ligands, and the first IP of the ion MX_k^- should be high. On the other hand, if the central atom of the anion has LPE (or unpaired electrons) and these electrons are involved in the ionisation, then as a consequence of the low EA of the M atom, the first IP of the MX_k^- ion will be comparatively low.

The influence of the additional electron on the electronic and geometric structure of a molecule MX_k depends on whether the M atom is a transition or non-transition element. In compounds MX_k, where k is the maximum valence of the M atom, the additional electron is generally accepted by an antibonding MO. If M is a non-transition atom, the ion MX_k^- is deformed in such a way that this electron becomes part of an LPE of the M atom (or in the case of radicals becomes the unpaired electron of the M atom). For example, if an electron is added to the linear BeF_2 molecule, the electron occupies an antibonding MO, and the BeF_2^- ion undergoes an angular deformation,[60] which decreases the antibonding action of this MO. In this case the additional electron becomes an unpaired electron of the Be atom.

In contrast to this, the geometry of the molecules and radicals of transition metals generally does not change when antibonding HOMO are filled with electrons. For example, in the series of hexafluorides from ReF_6^- to AuF_6^-, the antibonding HOMO $4t_{2g}$ is filled successively, but the geometry of the molecules remains octahedral.[61–63]

It is therefore appropriate to examine the systems MX_k separately for the cases where M is a non-transition element and where M is a transition metal.

1. Superhalogens Containing *sp*-Elements

According to the above ideas, in systems MX_k where k is smaller than or equal to the maximum valence of the atom M, an additional electron is accepted either by an antibonding MO or by a non-bonding MO of the central atom (that is forms part of an LPE of the M atom). In both cases the EA of the entire molecule or radical is low, because of the low EA of the M atom. The results of *ab initio* calculations with allowance for correlation[44,64,65] and experimental data[66,67] confirm this conclusion. On the other hand, in radicals of the type MX_{k+1}, where k is the maximum valence of the M atom, an additional electron enters a non-bonding MO of the ligands, to which the AO of the central atom does not contribute for symmetry reasons, and the delocalisation of this electron over ligands with high EA leads to a high EA for the radical.

According to calculations of the electronic structure of the radicals BeF_3, BF_4, MgF_3, AlF_4, SiF_5, PF_6 [56–58] and $BeCl_3$, BCl_4, $MgCl_3$, $AlCl_4$, $SiCl_5$, PCl_6 [68,69] by the discrete variation (DV) X_α method, the EA of these radicals is greater than 3.5 eV, and they can all be described as superhalogens. The same is true of systems $MX_{(k+1)/2}$, where X is a divalent oxygen atom, and k the maximum valence of the atom M. Estimates based on calculations of the electronic structure of the radicals BO_2, NO_3, AlO_2, PO_3, and ClO_4 [56–58] indicate that the EA of these systems are greater than 3.5 eV. Thus radicals of this type can also be described as superhalogens.

To emphasise the importance of high ligand EA values for the production of high EA in compounds MX_{k+1}, radicals whose HOMO are bonding can be considered. It might seem that in this case the ionisation potential from the HOMO of the anions MH_{k+1}^- should be fairly high; however, the estimated values of the first IP according to Koopmans (which, judging overall, are 1.0–1.5 eV too high) for BeH_3^-, BH_4^-, MgH_3^-, and AlH_4^- [70,71] are lower than those for the corresponding ions MF_{k+1}^-,[71,72] whose HOMO are non-bonding. The reason for this is evidently the low EA of the H atom.

It is thus possible to outline the range of molecules containing *sp*-elements which must undoubtedly be classified as superhalogens. These are radicals of the type MX_{k+1} where X is a halogen atom, and of the type $MX_{(k+1)/2}$, where X is an oxygen atom. Various other individual molecules can of course have fairly high EA. Examples are provided by the compounds $SeHal_6$ and $TeHal_6$,[73–75] which are of the type MX_k, where k is the maximum valence of the M atom. The additional electron in the ions MX_k^- occupies an antibonding HOMO, and the EA of the MX_k molecules should be low. This is the case, for example, for SF_6, whose EA is only 0.5–0.7 eV.[41,66] For SeF_6 and TeF_6, however, the EA is nevertheless fairly high (3.0 ± 0.2 eV and 3.34 ± 0.2 eV respectively).[76] This is related to the high polarity of the Se–F and Te–F bonds, as a consequence of which, although the HOMO have antibonding character with respect to the central atom–ligand interaction, the actual contribution to these MO from the AO of the central M atom is very small. In fact, the LUMO of SeF_6 and TeF_6 are non-bonding ligand MO, and this leads to high EA values for these molecules. It may be noted that the ions SeF_6^- and TeF_6^-, like the "metallic" octahedra MoF_6^- and WF_6^-, in which the additional electron again occupies antibonding HOMO, preserve the octahedral configurations.[77,78]

The difference in the EA values in the series of valence-isoelectronic molecules SF_6–SeF_6–TeF_6 has a marked influence on their chemical properties. Thus SF_6, which has a low EA, is stable in the gas phase, whereas SeF_6 and TeF_6, which have high EA, are not detected in the gas phase. On the other hand, the $SeCl_6^{2-}$ and $TeCl_6^{2-}$ anions form stable crystalline salts, whereas the corresponding salts with the SCl_6^{2-} anion have not been obtained.

In addition to SeF_6 and TeF_6, other molecules of the type MX_k, where M represents atoms of IV, V, and subsequent periods, may have fairly high EA. For example, the adiabatic EA, calculated by the DV-X_α method by the present authors, are 0.7 eV and 2.5 eV for the molecules PF_5 and SbF_5 respectively, and for AsF_5 the values lie in the range 1.9–2.9 eV. These are much lower than the values obtained from thermochemical data:[26] ~3.5 eV for PF_5, ≥ 5.3 eV for AsF_5, and ≥ 6.4 eV for SbF_5. The values given in Ref. 26 are apparently far too high. Further experimental studies of the EA of pentafluorides by up-to-date physical methods are required.

The EA of superhalogens of the type MX_{k+1} should increase with increase in k as a consequence of the delocalisation of the additional electron over a larger number of ligands. Thus in the series MgF_3 (~3.8 eV) < AlF_4 (~6.1 eV) < SiF_5 (~6.3 eV) < PF_6 (~6.6 eV) and AlO_2 (~3.4 eV) < PO_3 (~4.4 eV) < ClO_4 (~6.3 eV), the EA increases from 3.8 eV to 6.6 eV in the first case and from 3.4 eV to 6.3 eV in the second.[44] Extremal EA values should also be expected for MX_k with $k > 6$, but increase in k may also lead to a decrease in the EA. In particular, in the series $MgCl_3$ (~4.5 eV)–$AlCl_4$ (~5.2 eV)–$SiCl_5$ (~4.4 eV)–PCl_6 (~4.0 eV), beginning from $AlCl_4$ the EA decrease as a consequence of the strong repulsion of the ligands.[68,69] This last feature is related to the fact that the HOMO in the ions MX_{k+1}^- is non-bonding with respect to the central atom–ligand interaction, whereas with respect to the ligand–ligand interaction it has antibonding character. When *k* is sufficiently large, the mutual repulsion of the ligands predominates over the effect of electron delocalisation, leading to a decrease in the EA. For the optimum values of *k*, the effect of ligand–ligand antibonding is slight, and does not predominate over the delocalisation of the additional electron, and this leads to an increase in the EA. Of the superhalogens containing *sp*-elements which have been studied up to the present, the optimum ratio of antibonding and stabilisation is achieved for AsF_6 and SbF_6, which have high EA (~7 eV).[44]

The adiabatic EA is usually understood to be the difference between the total energies of the stable configurations of the anion and the neutral system. Available experimental data[40, 78–81] and the results of non-empirical calculations[82,83] indicate that the isolated anions MF_{k+1}^-, where *k* is the maximum formal valence of the central atom M, are energetically stable with respect to monomolecular dissociation to MF_k and F^-. Published estimates[78–83] of the energy of this dissociation are fairly high, 80–120 kcal $mole^{-1}$. At the same time, experimental data[84] indicate that MF_{k+1} radicals either have a very low energy of dissociation to MF_k + F or are generally unstable. It should be noted that the adiabatic EA of a radical can be determined even when it is unstable, since the necessary condition for the existence of EA is the existence of a stable negative ion. In this case the first IP_{vert} of the anion gives the upper limit of the EA_{ad} values of the neutral system.

The low energetic stability of MF_{k+1} radicals compared with the corresponding anions MF_{k+1}^- does not agree with the traditional ideas of the method of molecular orbitals, according to which the stability of a molecular system with respect to monomolecular dissociation should increase if the electron is removed from an antibonding MO, decrease if the electron is removed from a bonding MO, and remain unchanged if the electron is removed from a non-bonding MO. In all anions of the type MF_{k+1}^-, the highest occupied MO is non-bonding with respect to the central atom–ligand interaction, and consists only of ligand AO,[85] so that the removal of an electron from the HOMO of the anion should not lead to significant destabilisation of the resulting radical.

To investigate the reason for this discrepancy between the prediction based on the qualitative concepts of MO theory and available experimental data, the electronic structures of the anions BF_4^- and AlF_4^- and of the corresponding radicals BF_4 and AlF_4 were calculated by the discrete variation X_α method in the present work.

Data on the geometric structure are available only for the anions, and the calculated non-empirical equilibrium bond lengths in the isolated anions,[82] $R(B–F) = 1.43$ Å and $R(Al–F) = 1.72$ Å, are close to the corresponding values for the anions in inorganic salts:[86–88] $R(B–F) = 1.37–1.39$ Å and $R(Al–F) = 1.69–1.70$ Å. The equilibrium bond lengths in the anions, calculated by the DV-X_α method by the present authors, are $R(B–F) = 1.44$ Å and $R(Al–F) = 1.69$ Å, in good agreement with the above values. There are no published data on the geometric structure of the radicals BF_4 and AlF_4, so that their equilibrium bond lengths were optimised by the DV-X_α method assuming that they have a tetrahedral structure. The potential curves have minima in both cases, corresponding to the bond lengths $R(B–F) = 1.44$ Å and $R(Al–F) = 1.69$ Å. Thus the calculated bond lengths for the tetrahedral configurations of the radicals and anions practically coincide. The existence of minima on the potential curves of the radicals naturally does not mean that they are energetically stable with respect to monomolecular decomposition. To resolve the question of the stability of the radicals, it is necessary to carry out additional calculations of the total potential surfaces by non-empirical methods with allowance for correlation energy. These calculations cannot be carried out at present, because of the extremely large expenditure of machine time required. Although the present calculations do not make it possible to reach any conclusion about the stability of the radicals MF_{k+1}, they can be used to investigate the reasons for the destabilisation of these radicals.

The removal of an electron from a non-bonding MO of an anion should not in principle lead to destabilisation of the resulting radical if the composition of all the other MO remains unchanged. Since in the case being considered there is appreciable destabilisation of the radicals, it is natural to expect that this is the result of changes in the composition of the bonding MO as a result of electronic relaxation. The nature of the changes in the valence MO can be investigated using the data in Table 1, which gives the composition of these MO for both radicals and anions, for the equilibrium values of the bond lengths.

Table 1. Characteristics of the molecular orbitals of BF_4, BF_4^-, AlF_4, and AlF_4^-; the Mulliken populations of the bonding MO (*q*), the charges on the atoms (*Q*), and the overlap populations [*Q*(M–F)] for BF_4, BF_4^-, AlF_4, and AlF_4^- (in fractions of e).

Parameter	BF_4		BF_4^-		Parameter	AlF_4		AlF_4^-	
	B	ΣF	B	ΣF		Al	ΣF	Al	ΣF
$q(4t_2)$	0.22	5.78	0.26	5.74	$q(5t_2)$	0.37	5.63	0.48	5.52
$q(3t_2)$	1.03	4.97	1.11	4.89	$q(4t_2)$	0.63	5,37	0.72	5,28
$q(4a_1)$	0.39	1.61	0.40	1,60	$q(5a_1)$	0,36	1.64	0.36	1,64
Q_F	−0,23		−0.40		Q_F	−0.28		−0.45	
Q_B	+0.91		+0.61		Q_{Al}	+1.13		+0.78	
Q(B–F)	+0.47		+0,59		Q(Al–F)	+0,51		+0.62	
Q(F–F)	−0.05		−0.07		Q(F–F)	−0.01		−0.01	

It can be seen that the removal of an electron from the HOMO of the anion leads to a decrease in the contribution of the AO of the central atom to the bonding MO by ~0.3 e, and this explains the low stability of the radicals, compared with the corresponding anions. The reasons why ionisation from a non-bonding purely ligand HOMO of the anion leads to this rearrangement of electron density in the resulting radical can be understood on the basis of model representations of superhalogens in which the framework of fluorine atoms in the superhalogens has a high collective electronegativity. Thus if the process of ionisation of the anion is arbitrarily divided into two stages corresponding to the removal of an electron from the HOMO without change in the composition of any of the MO and the subsequent relaxation of the MO, then the loss of an electron by the framework of fluorine atoms in the first stage of the ionisation is partly compensated by the transfer of ~0.3 electron from the central atom.

A similar decrease in the energetic stability of the radicals compared with the corresponding anions should also be observed in all other systems of the type MF_{k+1} and MF_{k+1}^-.

2. Superhalogens Containing Transition Metals

In transition metal compounds of the type MX_k, the filling of antibonding HOMO generally does not lead to distortion of the geometry of highly symmetrical configurations, so that the behaviour of the EA of these systems may show a number of characteristic features.[89–94] The dependence of the EA on the electronic structure of transition metal hexafluorides can be considered in more detail. It is appropriate to begin the examination with the hexafluorides of the 5*d*-metals, since the characteristic features of the electronic structure are revealed most clearly in this case. Table 2 gives the IP from the valence MO. It can be seen that on going from Hf to Hg there is a change from the filling of a non-bonding purely ligand HOMO of the $1t_{1g}$ type (Hf, Ta) to the filling of an antibonding MO of the $4t_{2g}$ type, antibonding with respect to the central atom–ligand interaction (W–Au) and then to the filling of the next antibonding MO of the $6e_g$ type (Hg).

Table 2. Valence ionisation potentials (eV) of the negative ions of the hexafluorides of metals of the third transition series.[90]

MO	Spin*	HfF_6^-	TaF_6^-	WF_6^-	ReF_6^-	OsF_6^-	IrF_6^-	PtF_6^-	AuF_6^-	HgF_6^-
$6e_g$	—	—	—	—	—	—	—	—	—	4.5
$4t_{2g}$	l h	— —	— —	2.2 —	3.5 —	4.7 —	5.9 4,5	6.1 5.6	6.8	7.6 7.2
$1t_{1g}$	l h	7.5 6,8	7,1	7.3 6.9	7.1 6.7	7.6 6.6	7.4 6.6	7.2 6.7	6.9	7,3 7.0
$9t_{1u}$	l h	7.3 6.8	7.3	7,7 7.3	7.6 7.2	7.7 7.1	7.9 7.1	7.5 7.1	7.3	8,0 7.3
$2t_{2u}$	l h	8.0 7.2	7,5	7.5 7.3	7.8 7.3	8.0 7.2	7.9 7.1	7.7 7.2	7.4	7.8 7.5
$8t_{1u}$	l h	8.3 7.5	8.0	8.1 7.9	8.4 7.9	8.7 7.9	8.6 8.0	8.5 8.1	8.2	9.0 8.5
$8a_{1g}$	l h	8.3 8.2	8.0	8.1 8.7	8.4 8.7	8.7 8.8	8.6 8.9	8.5 9.0	8.2	9.0 9.5
$3t_{1g}$	l h	9.9 9.3	10.1	10.5 10.0	11.3 10.2	12.1 10.2	12.2 10.9	12.4 12.0	13.4	16.3 15.7
$5e_g$	l h	10.3 9.9	10.6	11.0 10.6	11.5 10.7	12.5 10.9	12.2 11.4	12.5 12.1	13.6	17.2 17.0

*The letters l and h denote transitions into the low-spin and high-spin final states of MF_6 respectively.

The data in Table 2 reveal the following characteristic features of the change in the IP from the valence MO in the series being considered. Firstly, it is irregular : the IP decreases sharply on going from TaF_6^- to WF_6^-, after which it increases regularly from WF_6^- to AuF_6^-, and decreases again on going to HgF_6^-. Secondly, the IP of the "ligand" $1t_{1g}$–$8a_{1g}$ MO remain practically unchanged. Thirdly, the IP from the bonding $3t_{2g}$ and $5e_g$ MO increase almost regularly, although the change in their energies on going along the series is smaller than the change in the energies of the 5d AO [90,92] of the corresponding central atoms.

The reason for this behaviour of the IP can be understood by analysing the composition and symmetry of the MO. For Hf and Ta hexafluorides, the HOMO is a non-bonding ligand orbital, and the EA of these compounds is high as a consequence of the delocalisation of the additional electron over the six strongly electronegative F atoms, in accordance with the above ideas on the superhalogens containing *sp*-elements. The EA of these two hexafluorides are close to the EA of the most electronegative superhalogens among compounds of the *sp*-elements: AsF_6 and SbF_6. On going to WF_6, the EA decreases, due to the filling by electrons of a HOMO of antibonding type; the energy gap between the nearest $4t_{2g}$ and $1t_{1g}$ MO is ~4 eV. Since the $4t_{2g}$ MO is antibonding, it might have been expected that its subsequent filling would lead to a decrease in the EA in the series being considered. Instead of this, however, there is a regular increase in the EA,[90] which reaches ~7 eV for AuF_6, and the gap between the $4t_{2g}$ and $1t_{1g}$ MO practically disappears.

The composition of the $4t_{2g}$ MO can be analysed in more detail. The nature of this orbital changes in the hexafluoride series[90] from appreciably antibonding (WF_6^-) to non-bonding (AuF_6^-). With decrease in the antibonding, its energy decreases, approaching the energy of the non-bonding MO of the ligands ($1t_{1g}$, $9t_{1u}$, $2t_{2u}$), and the EA for AuF_6 is close to the EA for TaF_6, in which the additional electron occupies a $1t_{1g}$ MO which is purely ligand from symmetry. On going from AuF_6^- to HgF_6^-, the next $6e_g$ MO is filled, accompanied by a decrease in EA, due chiefly to the extensive splitting of the $6e_g$–$4t_{2g}$ orbitals under the influence of the ligand field, since the $6e_g$ MO is essentially a ligand orbital. Thus the contribution of the 5*d* AO to the $6e_g$ MO is ~25%, and practically coincides with the contribution of the 5*d* AO to the $4t_{2g}$ MO of the AuF_6^- anion.[90] At the same time, an increase in the Hg–F overlap population is observed for HgF_6^-, compared with AuF_6^-.

It is of interest to relate the change in the EA in the series of hexafluorides Hf–Hg to the energy of the atomic 5*d* levels. On going along this series, the energy of the 5*d* AO decreases,[90,92] leading to stabilisation of the $3t_{2g}$ and $5e_g$ MO, and these MO are transformed to an increasing extent into non-bonding 5*d* AO. In other words, the 5*d* electrons tend to be localised close to the central atom M, leading to a decrease in the population of the 5*d* AO in the higher orbitals $4t_{2g}$ and $6e_g$ and to the approach of the $4t_{2g}$ MO to the ligand MO. This conclusion is confirmed by the decrease in the overlap population from WF_6^- to AuF_6^- and by its increase on going to HgF_6^-, since in this case the 5*d* electrons, for symmetry reasons, are forced to partly occupy the antibonding $6e_g$ MO.

The principal features of the electronic structure are the same for the hexafluorides of the 4*d* metals and the hexafluorides of the 5d metals, but some differences are also observed. Firstly, the block of valence MO of the ligand type for the hexafluorides of the 4*d* metals on the whole lie slightly higher (by 0.3–0.5 eV) than those for the 5d metals. This agrees with available experimental data on the IP of the compounds MoF_6 and WF_6,[30] which differ by ~0.3 eV. Moreover, the HOMO of the t_{2g} type for MoF_6^- lies 1.3 eV closer to the block of valence MO than in the case of WF_6^-, as a result of which the EA for MoF_6 is ~1 eV higher. The calculated differences between the IP of the $4t_{2g}$ and $1t_{1g}$ levels for WF_6^- and the IP of the $3t_{2g}$ and $1t_{1g}$ levels for MoF_6^- agree with the difference between the energies of the first optical transitions for the compounds MoF_6 and WF_6 [$\Delta\nu_1(WF_6) - \Delta\nu_1(MoF_6) = 1.33$ eV [95]]. The lower energy of the upper t_{2g} MO in MoF_6^- compared with WF_6^- is related to the lower degree of antibonding character of this MO, and this in turn is due to the higher energy of the 4*d* AO of the Mo atom.[90,92]

With further filling of the HOMO of the t_{2g} type, the degree of antibonding character of this MO in the 4*d* hexafluorides is again lower than in the 5d hexafluorides, leading to its more rapid approach to the block of ligand MO. Moreover, for AgF_6^-, where the $3t_{2g}$ HOMO is fully occupied, the energy of this MO is lower than the energies of the purely ligand $1t_{1g}$ and $1t_{2u}$ MO. For AuF_6^-,[90] this inversion of the levels is not observed. The sequence order of the MO in AgF_6^- does not agree with the traditional picture of the energy sequence for MO of different character (see above): ε(bonding) > ε(non-bonding) > ε(antibonding). This contradiction is eliminated, however, in a more detailed analysis of the nodal structure of the valence MO, represented schematically in Fig. 2. It can be seen that the $3t_{2g}$ MO is an antibonding MO of the π-type with respect to the central atom–ligand interaction, and a bonding MO of the σ-type with respect to the ligand–ligand interaction; the $1t_{1g}$ MO is σ-antibonding and purely ligand from symmetry; and $7t_{1u}$ and $1t_{2u}$ MO are orbitals of the π-type, and the first contains a small contribution from the central atom, whereas the second is a purely ligand antibonding MO.

On going from MoF_6^- to AgF_6^-, the contribution of the M atom to the $3t_{2g}$ MO decreases sharply, and in AgF_6^- the entire block of $3t_{2g}$–$1t_{2u}$ MO can be regarded as purely ligand, and the central atom–ligand interaction can be neglected.[92] In this case, from the ligand–ligand interactions and in accordance with classical ideas, the following sequence of MO energies can be expected: $3t_{2g}$ (bonding MO of the σ-type) > $7t_{1u}$ (antibonding, π-type) > $1t_{2u}$ (antibonding, π-type) > $1t_{1g}$ (antibonding, σ-type). This MO sequence is in fact observed for AgF_6^- and CdF_6^-, that is the electronic structure of the hexafluorides at the end of the 4*d* metal series is determined by purely ligand interactions.

The principal characteristic features of the change in the EA and IP in the series of 3*d* metal hexafluorides are on the whole the same as in the series of 4*d* and 5*d* metal hexafluorides,[90,92] although they are less clearly defined. In particular, the antibonding HOMO of the $2t_{2g}$ type in CrF_6^- lies only 1.5 eV above the block of purely ligand MO, whereas the corresponding values for the $3t_{2g}$ and $4t_{2g}$ MO in MoF_6^- and WF_6^- are 3.8 eV and 5.1 eV respectively. On further filling of the $2t_{2g}$ MO in the anions of the 3*d* element hexafluorides, its energy rapidly approaches the energies of the ligand MO, and inversion with respect to the $1t_{1g}$ MO takes place at FeF_6^-, whereas the corresponding inversion of the $3t_{2g}$ and $1t_{1g}$ MO is observed only at the end of the 4*d* series, for AgF_6^-. This behaviour of the $2t_{2g}$ MO is related to its lower antibonding character, compared with the $3t_{2g}$ MO for the 4*d* element hexafluorides, resulting from the higher energies of the 3*d* AO of the atoms in the first transition series. A decrease in the antibonding character of the HOMO of the t_{2g} type with increase in the energy of the atomic *d*-orbitals was also observed on going from the hexafluorides of the 5*d* elements to the hexafluorides of the 4*d* elements, although to a smaller extent than on going from the hexafluorides of the 4*d* elements to the hexafluorides of the 3*d* elements. In this connection it should be noted that small changes in the energies of the atomic *d*-orbitals lead to fairly large changes in the energies of HOMO of the t_{2g} type. The small contribution of the central atom to the HOMO of the hexafluorides of the 3*d* elements leads to high values (6–7 eV) of the EA for the entire series (with the exception of CrF_6, whose EA is also fairly high, 5.0–5.5 eV).

The above detailed analysis of the relationship between EA and electronic structure shows that the hexafluorides of the *d*-elements differ significantly from the fluorides of the *sp*-elements; practically all transition metal hexafluorides (with the possible exception of WF_6) can be regarded as superhalogens. At the same time, the dependence of the value of the EA on the electronic structure in each specific case is fairly complex. Nevertheless, it can be stated that among the hexafluorides of the 4*d* and 5*d* metals, the highest EA will be shown by those in which the HOMO is almost completely filled (that is NbF_6, TaF_6, AgF_6, and AuF_6). The hexafluorides of the 3*d* metals almost all have high EA.[44]

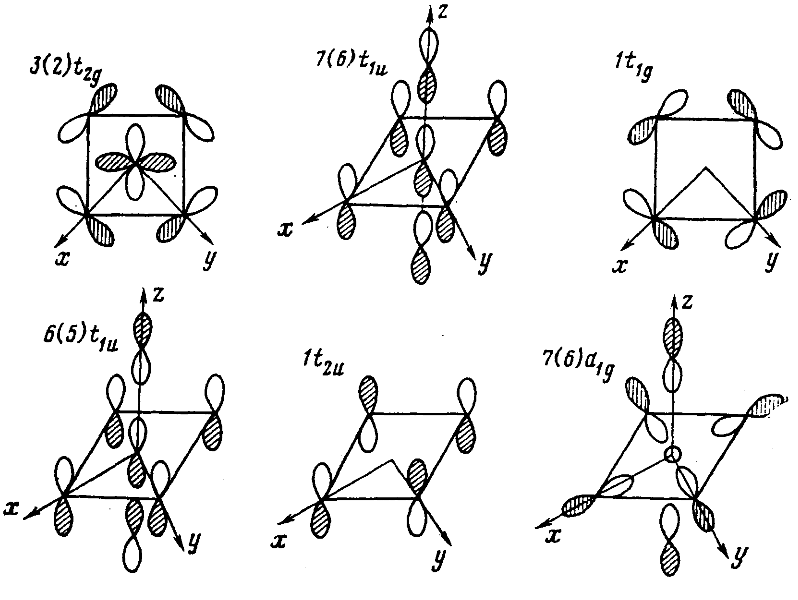

Figure 2. Schematic representation of the highest valence MO of transition metal hexafluorides.[92]

As noted above, in the estimation of EA_{ad} for systems in which the additional electron enters an antibonding MO it is necessary to investigate the dependence of the first IP_{vert} of the anion on the M–F bond length. To investigate this relationship, the electronic structure of the anions CrF_6^- and AgF_6^- has been calculated.[92] The distances R(Cr–F) = 1.75 Å and 1.85 Å and R(Ag–F) = 1.85 Å and 1.98 Å were used in the calculations. The calculations showed that the change in the IP from the HOMO of CrF_6^- does not exceed 0.5 eV, and that from the HOMO of the anion AgF_6^- does not exceed 0.15 eV. It may therefore be expected that for other transition metal hexafluorides, small changes in the interatomic distances will not lead to changes in the EA value exceeding 0.5 eV. The influence of R(M–F) on the EA value is a maximum for the atoms of group VI, since the HOMO of their hexafluorides has the most antibonding character with respect to the central atom–ligand interaction, and decreases in the same sense as the decrease in the antibonding towards the end of the period.

Tetra-anions MX_4^-, where X = F, O, and Cl, are also encountered in salts. It is therefore of interest to study the dependence of the EA of these anions on the characteristic features of their electronic structure. The tetraoxyanions can be considered as an example. The orbital energies of the tetraoxyanions of the 4*d* metals are given in Table 3. The following characteristic features of the change in the IP from the valence MO can be observed on going along the series. Firstly, the change is irregular: the IP value decreases on going from TcO_4^- to RuO_4^-, then increases from RuO_4^- to AgO_4^-, and decreases again on going to CdO_4^-. Secondly, the IP of the block of "ligand" $1t_1$, $8t_2$, and $7a_1$ MO remain practically unchanged on going along the series, like the IP of the $6t_2$ and $6a_1$ orbitals, formed predominantly by the 2*s* orbitals of the O atom. Thirdly, the IP of the bonding $7t_2$ and $2e$ MO increase regularly along the series.

Table 3. One-electron energies (eV) of the valence MO of 4*d*-metal tetraoxyanions.[94]

Anion (configuration)	MoO_4^- ($1t_1^5$)		TcO_4^- (closed)	RuO_4^- ($3e^1$)		RhO_4^- ($3e^2$)		PdO_4^- ($3e^3$)		AgO_4^- (closed)	CdO_4^- ($9t_2^1$)	
Spin	α	β	α=β	α	β	α	β	α	β	α=β	α	β
$9t_2$	—	—	—	—	—	—	—	—	—	—	3.4	—
$3e$	—	—	—	3.1	—	3.8	—	4.1	3.5	4.4	4.4	4.3
$1t_1$	5.6	4.8	4.9	4.8	4.5	5.1	4.2	4.8	4.2	4.7	4.5	4.3
$8t_2$	5.8	5.4	5.5	5.5	5.2	5.7	5.0	5.5	5.1	5.4	5.5	5.0
$7a_1$	6.2	5.8	6.2	6.0	5.8	6.0	5.6	5.8	5.5	5.8	6.3	5.5
$7t_2$	8.3	8.0	8.7	9.0	8.8	9.3	9.2	10.2	10.1	12.4	15.6	15.3
$2e$	8.3	7.9	8.5	9.0	8.7	10.0	9.3	10.7	10.5	13.6	17.8	17.8
$6t_2$	20.9	20.3	20.5	20.4	20.1	20.7	19.9	20.4	20.1	20.4	20.6	20.1
$6a_1$	21.1	20.5	20.6	20.6	20.2	20.7	20.0	20.5	20.1	20.5	21.0	20.6

Overall, the characteristic features of the change in the valence IP in the series of oxyanions are approximately the same as in the hexafluoride series. A difference is that in the tetraoxyanions, a HOMO of the *e* type is filled first, and the filling of the antibonding MO of symmetry t_2 begins from CdO_4^-. Moreover, the actual EA values for the tetra-oxides and their abrupt changes on going to the filling of antibonding MO of the *e* and t_2 types are appreciably smaller than for the hexafluorides. The changes in the upper valence IP on going along the series of 3*d* metal tetraoxyanions are similar to the changes in the upper valence IP in the series of 4*d* metals. As in the case of the hexafluorides of the 3*d* and 4*d* metals, however, the actual EA values for the tetra-oxides of the 3*d* metals are greater, and the abrupt changes on going to the filling of the antibonding MO are smaller, than in the case of the tetra-oxides of the 4*d* metals. On the whole, the EA values for the tetra-oxides are greater (3.5–5.0 eV), and practically all transition metal oxyanions, with the possible exception of RuO_4, can be classified as superhalogens.

A similar analysis of the dependence of the EA on electronic structure can be carried out for pentafluorides MF_5, tetrafluorides MF_4, trifluorides and trioxides MX_3, difluorides and dioxides MX_2, etc. High EA are shown not only by superhalogens of the type MX_{k+1}, where k is the maximum formal valence of the metal and X is a monovalent ligand, but also by systems of the type MX_k if the antibonding HOMO of the corresponding anion is completely or almost completely filled.

3. The Search for Systems with the Maximum Possible Electron Affinity

Theoretical studies of superhalogens and various experimental estimates show that chemical compounds may have very high EA, exceeding the EA of halogen atoms. Two questions naturally arise: what is the maximum EA that superhalogens can have, and among which systems should they be sought? According to the above ideas, these systems should contain as ligands the maximum possible number of fluorine atoms, since the energy of the HOMO of the anions of these systems would approach the energy of the HOMO of neutral fluorides, as a consequence of the delocalisation of the additional electron over a large number of ligands. Thus the value of the first IP of neutral fluorides can be regarded as the upper limit of the maximum possible EA values. According to available experimental data, the first IP in the fluoride series SF_6, WF_6, SiF_6, CF_4,[30] etc. are 15–17 eV, so that the value 17 eV can be taken as the upper limit of EA values for chemical compounds.

Various ways of searching for systems with maximum EA may be noted. One way is to increase the number of ligands in mononuclear systems of the type MF_{k+1}. However, with increase in the number of ligands, beginning from a certain value of k, the effects of destabilisation of the HOMO of the ion MF_{k+1}^- as a result of inter-ligand repulsion may predominate over the stabilising effects of delocalisation, so that further increase in the EA will not take place, as for example in the chlorides of the *sp*-elements examined above. Another possible way to increase the number of ligands is by changing to polynuclear superhalogens, of the type Al_2F_7, Sb_2F_{11}, or in general M_nX_{nk+1}. In these systems, inter-ligand repulsion does not increase with increase in the number of ligands, and as a result of the maximum delocalisation of the electron, the EA of these systems may approach the maximum possible value. These ideas are of course qualitative, and indicate only the trends in the change in the EA, and to obtain quantitative estimates it is necessary to carry out calculations for each specific case.

To follow the trend in the change in the EA with increase in the number of ligands, it is possible to use the results of calculations by the DV-X_α method of the electronic structure of the anions MnF_8^- and TcF_8^- (mononuclear anions of the type MF_{k+1}^-) and $Al_2F_7^-$, $P_2F_{11}^-$, $As_2F_{11}^-$, and $V_2F_{11}^-$ (dinuclear anions of the type $M_2F_{2k+1}^-$).[96,97] The geometric structure of the dinuclear anions is shown in Fig.3.

In the series of mononuclear anions ScF_4–VF_6–MnF_8, the EA increases sharply on going from ScF_4 (4.8 eV) to VF_6 (6.7 eV), and then remains unchanged on going from MnF_8

(6.7 eV). On going from NbF_6 (6.8 eV) to TcF_8 (5.8 eV), it even decreases. This indicates that the optimum combination of stabilising and destabilising factors to achieve the highest EA values in mononuclear complexes is obtained in the six-coordinate fluorides. Further increase in the number of ligands does not lead to an increase in the EA, because of the increase in the strength of the inter-ligand repulsion. Calculations by the DV-X_α method indicate that the maximum EA in mononuclear complexes (TaF_6 and AuF_6) is 7–8 eV.[90]

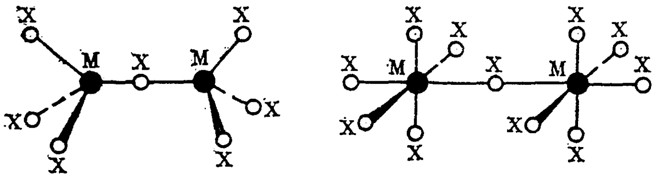

Figure 3. Geometric structure of dinuclear superhalogens.

On going from the mononuclear to the corresponding dinuclear complexes, the EA increases systematically by 1–2 eV. Thus for example the EA values for AlF_4 and Al_2F_7 are 6.1 eV and 7.5 eV, for PF_6 and P_2F_{11} 6.7 eV and 8.6 eV, for AsF_6 and As_2F_{11} 7.2 eV and 8.6 eV, and for VF_6 and V_2F_{11} 6.7 eV and 8.0 eV respectively.[90] Thus the maximum EA for dinuclear systems is apparently 9–10 eV. In particular, these EA values may be shown by the systems Ta_2F_{11} and Au_2F_{11}. Thus the change from mononuclear to polynuclear superhalogens is a promising way of searching for systems with the maximum possible EA values. Polynuclear superhalogens whose EA are more than twice the EA of halogen atoms should rather be called hyperhalogens. They may be used to obtain new classes of salt with non-traditional cations. Stable salts with Ar^+ cations may possibly be obtained using complex polynuclear hyperhalogens.

Table 4. Theoretical estimates of the EA of various superhalogens, obtained by the DV-X_α method*.[44]

Radical	EA, eV	Radical	EA, eV	Radical	EA, eV
BeF_3	4.1 (4.5)	PdF_6	6.1	TcF_8	5.8
MgF_3	3.2 (3.8)	AgF_6	6.4	Al_2F_7	7.5
BF_4	6.2 (6.2)	CdF_6	4.8	P_2F_{11}	8.6
AlF_4	6.1 (6.2)	AsF_6	7.2	As_2F_{11}	8.6
SiF_6	6.4 (6.3)	SbF_6	7.0	V_2F_{11}	8.0
PF_6	6.8 (6.6)	HfF_6	8.8	MoO_4	6.2
TiF_6	7.5	TaF_6	8.4	TcO_4	4.9
VF_6	6.7	$BeCl_3$	4.5 (4.2)	RuO_4	3.1
CrF_6	5.0	BCl_4	4.9 (4.5)	PhO_4	3.8
MnF_6	5.9	$MgCl_3$	4.5 (4.5)	PdO_4	4.7
FeF_6	7.0	$AlCl_4$	5.8 (5.0)	AgO_4	4.4
CoF_6	6.8	$SiCl_5$	4.9 (4.2)	CdO_4	3.4
NiF_6	6.9	PCl_6	4.3 (3.7)	CrO_4	6.1
CuF_6	6.1	SCl_6	3.4	MnO_4	5.0
ZnF_6	5.8	$SeCl_6$	4.3	FeO_4	3.7
ZrF_6	7.1	$TeCl_6$	3.5	CoO_4	5.2
NbF_6	6.8	$SbCl_6$	5.6	NiO_4	4.7
TcF_6	4.3	$AsCl_6$	5.4	CuO_4	4.4
RuF_6	5.2	VF_4	4.8	ZnO_4	3.9
RhF_6	6.1	MnF_6	6.7	HgF_6	5.8

*The values in brackets were calculated in a two-exponent Clementi basis set with the addition of polarisation functions of the central atom.

Finally, Tables 4–6 summarise available theoretical and experimental estimates of the EA of superhalogens.

Table 5. Theoretical and experimental estimates of the EA (eV) of various superhalogens.

Compound	Experimental estimate	Calculation by the DV-X_α method	Calculation by the DV-X_α method; HF (DE) basis set
BO_2	3.6±0.2 [40]	—	4.6 (3,6) [56]
AlO_2	4,1±0.2 [40]	—	3,7 (3,4) [56]
NO_3	3,68±0.20 [66]; 3,77±0,25 [41]	—	4.0 (3,6) [56]
PO_3	4.9 [99]	—	5.3 (4,4) [56]
ClO_4	5,8 [67]; 6.2 [100]	6,9 [98]	6.9 (6,3) [56]
SF_6	0.30 [41]; 0.75 [66]	0,5 [101]; 0.7 [102]	0.3 (0,6) [73]
SeF_6	3.0±0.2 [76]	2.9 [102]	2.1 (3,0) [73]
TeF_6	3.34±0.2 [76]	2.6 [102]	1.2 (2.2) [73]
MoF_6	5,14 [76]; 3.6±0,2 [103]; 5,36±0.06 [104]; 4.5 [105]; 5,77 [106]	4.5—4.8 [101]	3.2 [92]
WF_6	3,51±0.10 [40]; 4.9 [105], 3.7 [107]; 5,1±0,5 [76]; 3.36 [108]; 3.5 [26]	4.5—5.1 [101]	3,5 [90]
ReF_6	4,6 [26]	5.3—6.3 [101]	4.8 [90]
OsF_6	5,9 [26]	6.2—7.3 [101]	6.0 [90]
IrF_6	4.34 [67]; 5.1±0,5 [76]; 7.0 [26]	7,0—8.3 [101]	7,2 [90]
PtF_6	5.1—7.9 [109]; 8,2 [26]	7,9—9.1 [101]	7,4 [90]
AuF_6	—	8,4—10.1 [101]	8,1 [90]
UF_6	4.9±0.5 [110]; 5.0 [111]; 3.6 [79]; 4,3 [112]; 5,1; 4,85±0.25; 5.60±0.25 [113]	5.0 [101]	—

Note. Numbers in square brackets denote references (Ed. of Translation).

Table 6. Experimental estimates of the EA of various superhalogens.

Radical	EA, eV	Refs.	Radical	EA, eV	Refs.
MnF_3	5,27±0,20	[111]	CrO_3	3.7	[114]
FeF_3	4,25±0,20	[111]	$MoOF_4$	4.0±0.4	[103]
PtF_3	2.1	[109]	UF_5	3.5	[113]
MnF_4	5.22	[109]	U_2F_9	4.2±0.5	[115]
FeF_4	5.40±0.20	[111]	U_2F_{10}	4.5±0.4	[115]
PtF_4	5.11±0.36	[109]	U_2F_{11}	6.1±0.7	[115]
PtF_5	6.5	[109]	U_2F_{12}	7.9±0.8	[115]

4. Characteristic Physicochemical Properties of Superhalogens

Molecules with high EA show a whole series of fundamentally important distinguishing properties. Thus the high EA of $SeCl_6$ and $TeCl_6$ makes possible the existence of the anions $SeCl_6^{2-}$ and $TeCl_6^{2-}$, which are unusual from the traditional chemical viewpoint.

A high EA makes it possible to obtain fundamentally new salts with unusual cations, such as $O_2^+[PtF_6]^-$, $XeF_5^+[PtF_6]^-$, $Xe_2F_{11}^+[AuF_6]^-$, etc.[1–12] The molecules O_2, XeF_5, and Xe_2F_{11} have high IP, so that to obtain salts with their cations it is necessary to use superhalogens with anomalously high EA, such as, for example, PtF_6, AuF_6, etc. Thus superhalogens open up extensive possibilities for the synthesis of new non-traditional salts with both organic and inorganic cations.

Another unusual property of systems containing superhalogen groups is related to the high IP of the anions of superhalogens. Compounds in the gas phase in most cases dissociate homolytically, to give a pair of neutral fragments. This rule may not extend to molecules containing superhalogens, however. Thus the values of the IP of the alkali metals are 3.9–5.4 eV, and the EA of superhalogens may exceed these values. In these cases, heterolytic dissociation may be more favourable. For example, the salt Cs–AlF_4

dissociates to Cs^+ and AlF_4^-, and not to Cs and AlF_4. This heterolytic dissociation makes it possible to obtain a low-temperature molecular plasma by simple heating, and this in turn ensures increased conductivity of the vapours of these salts. The gas-phase mixtures of $NaAlCl_4$ and $KAlCl_4$ with $AlCl_3$–Al_2Cl_6 [116] have electrical conductivity values which are fairly high for gases, amounting to 10^{-11}–10^{-6} Ω^{-1} cm^{-1} in the temperature range 500–900 K. The partial pressure of ions in the gas reaches 10^{-8} atm at a partial pressure of $NaAlCl_4$ of 0.1 atm.

Superhalogens are widely used to modify the electronic characteristics of one-dimensional and two-dimensional organic compounds to obtain materials with metallic conductivity, and also organic superconductors.[14–26] All organic superconductors obtained up to the present contain superhalogens anions as counter-ions. It is suggested that the geometric structure of the anion is important for the conversion of quasi-one-dimensional organic systems to the superconducting state.[18] Thus for the synthesis of new organic superconductors with a higher critical temperature T_c it is necessary to have a wide range of superhalogens with different geometric structures.†

On the other hand, the class of counter-ions suitable for obtaining organic superconductors can be extended considerably using the cations of superalkalies, since the quasi-one-dimensional stacks of organic conjugated molecules forming the starting material have not only donor but also acceptor properties. The synthesis of organic systems using superalkali cations as counter-ions would extend considerably the range of organic semiconductors, metals, and superconductors, and would also be extremely interesting for theoretical chemistry.

IV. ELECTRONIC STRUCTURE OF SUPERALKALIES

After the detection of the large class of molecular systems having high EA (superhalogens) there arose the question, which is important for extending the concept of electronegativity and electropositivity, of the lowest possible IP values of neutral molecules and radicals, that is the EA of the corresponding singly charged cations. Among the elements of the periodic system, the lowest first IP are shown by alkali metal atoms, so that systems whose first IP are lower than those for alkali metal atoms are naturally called superalkalies.

From the ideas presented in section II, it follows that to achieve a low first IP of a neutral system of the type ML_{k+1}, it is necessary that the HOMO be antibonding with respect to the central atom–ligand interaction, and, in addition, that the ligands have low upper IP. In this case, on formation of the compound ML_{k+1}, the electrons of the L atoms will enter an antibonding MO, and the energy of their bond in the ML_{k+1} molecule will be lower than in the isolated L atom. It should therefore be promising to look for "superalkalies" in the class of systems ML_{k+1}, where L are alkali metal atoms.

To verify this suggestion, the DV-X_α method was used[117,118] to calculate the electronic structure of a number of radicals of this type. Table 7 gives the results of the calculation of the first IP of radicals ML_{k+1}, and also available experimental estimates. The IP of the radicals were calculated for the equilibrium geometry of the corresponding cations, that is the values of the first IP of the radicals ML_{k+1} given in Table 7 are equal to EA_{vert} for the cations ML_{k+1}^+. Clementi's double-exponent (DE) basis set was used in the calculations.[117,118] It was shown for the typical superalkalies $ClNa_2$ and PNa_4 that expansion of the DE basis set by including polarisation (3*d*) and diffuse (3*s*, 3*p*) functions of the central atom, and also polarisation (3*p*) functions of the ligand atoms, leads to only slight changes (~0.1 eV) in the first IP and the composition of the HOMO.

Table 7. First ionisation potentials (eV) of superalkali radicals.

Radical	Experiment	Calculation (Refs.117,118)
FLi_2	—	3.6
$ClNa_2$	4,15±0.20 [119]	3.7
FNa_2	—	3.7
FCs_2	—	2,6
$ClCs_2$	—	2,3
OLi_3	4,54±0,20 [120]	3.4*
ONa_3	3,90±0.15 [121]	3.5
OK_3	3,65±0.04 [121]	—
ONa_4	3,95±0.10 [121]	—
OK_4	3.62±0.04 [121]	—
SLi_3	—	3,2
SNa_3	—	3,3
NLi_4	—	3.6
NNa_4	—	3.7
PLi_4	—	3.0
PNa_4	—	3.2
NH_4^{**}	4,6 [125] 4,73±0,06 [126]	4.1

Non-empirical calculation with allowance for correlation energy (MP2/6-311) [122] gives the value 3.37 eV.

**See Ref. 123 and references therein up to 1984; non-empirical calculation with allowance for correlation energy[124] (SDFI) gives the values IP_{ad} = 4.41 eV and IP_{vert} = 4.43 eV.

Note. Numbers in square brackets denote references (Ed. of Translation).

The coefficients of the LCAO expansion of the valence MO in the DE basis set for the radicals FLi_2, OLi_3, and NLi_4 are given in Ref. 118. The MO have a similar structure for other radicals of corresponding types. According to Ref. 118, the doubly occupied MO consist chiefly of the AO of the central atom, whereas the highest half-filled MO consist chiefly of the AO of the ligands. For these radicals, the HOMO are antibonding with respect to the central atom–ligand interaction, and according to traditional views of the structure of MO its energy should be higher than the energies of the AO of both the central atom and the ligands. In fact, in all cases the IP of the radicals (see Table 7) are lower than the IP of the alkali metal atoms, which lie in the range 3.9–5.4 eV for Cs–Li. Thus the ML_{k+1} cations being considered must be regarded as superalkalies, since the first IP of the corresponding radicals are lower than the first IP of alkali metal atoms.

The above radicals were chosen so that it would be possible to follow the change in the IP with change in the ligand L and the central atom along a sub-group, and also with increase in the number of ligands. The replacement of Li by Na leads to small changes in the IP, and no regular trends could be established from the results of the calculations. The replacement of Na by Cs in the series FNa_2–FCs_2 and $ClNa_2$–$ClCs_2$, however, leads to a significant decrease in the IP. When a ligand is replaced by a heavier ligand from the same sub-group, a decrease in the EA of the corresponding cation should apparently be expected. The replacement of the

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†In view of the importance of the tetrahedral structure of the counter-ion for increasing T_c (for example ClO_4^- [18]), the anions of transition metal tetra-oxides can be recommended as counter-ions for the production of new superconductors.

central atom by a heavier atom from the same sub-group will also lead to a decrease in the EA, although the relative changes are small. With increase in the number of ligands in series of the type FLi_2^+–OLi_3^+–NLi_4^+, the EA on the whole decreases, although the decrease is small. For the EA of the cation to be small, it is not necessary that the IP of the ligands be low. If the antibonding of the HOMO is strong, the energy of the binding of an electron in the neutral system ML_{k+1} may be low, in spite of a high EA for the cation L^+.

Another type of molecular radical ML_{k+1} with low values of the first IP may be provided by Rydberg radicals, in which the additional (relative to the corresponding cation) electron enters a Rydberg AO of the central atom. In this case, since the Rydberg AO of the M atom are fairly high, the IP from these AO should be low. An example of these systems may be provided by ammonium radicals NR_4, where R is an organic group. For the simplest system NH_4, detailed *ab initio* calculations have been carried out with variation of the geometry of the cation NH_4^+ and the radical NH_4 separately, and with allowance for the correlation energy by the configuration interaction method with the addition of Rydberg orbitals to the basis set.[127] These calculations showed that the HOMO in NH_4 consist chiefly of the Rydberg AO of the N atom, and the value of IP_{ad} for the NH_4 radical (or EA_{ad} for the NH_4^+ cation) is 4.3 eV. This value shows good agreement with the experimental estimates 4.6 ± 0.2 eV [125] and 4.73 ± 0.06 eV.[126] Other radicals NR_4 for which R has electron-donor properties should have even lower IP, and all these radicals can apparently be classified as alkalies or superalkalies.

Both superalkalies and Rydberg radicals are stable with respect to monomolecular dissociation,[119–126] although the dissociation energy is relatively low. At the same time the corresponding cations are extremely stable with respect to monomolecular dissociation. Thus the dissociation energy of $ONa_3^+ \rightarrow ONa_2 + Na^+$ is 87 kcal mole^{-1},[122] and that of $NH_4^+ \rightarrow NH_3 + H^+$ is 217 kcal mole^{-1}.[124]

The low EA of "superalkali" cations indicates the possibility of synthesising new classes of salt in which the anions are molecular systems with low EA. The first salts of this type, $LiO_3^+NO^-$ and $Li_3O^+NO_2^-$, have already been synthesised, and X-ray diffraction has confirmed that they contain Li_3O^+ cations.[27–29] Superalkali cations can form salts in cases where the formation of the corresponding salts with alkali metal atoms may be energetically unfavourable either because of the relatively high IP of the metal atom or because of steric hindrance. Salts consisting of superalkali cations and superhalogen anions can apparently have very low heterolytic dissociation energies, and this is of interest from the viewpoint of the physics of low-temperature molecular plasma.

In recent years, *ab initio* calculations have revealed a new class of so-called hyperlithium compounds OLi_4, OLi_5, CLi_5, CLi_6, etc.[128–132], in which the formal valence of the central atom is greater than the maximum classical valence. According to the calculations, the first IP of these compounds are relatively low, and these systems can also apparently be regarded as superalkalies. The question of the existence and energetics of hyperlithium compounds requires further theoretical and experimental studies, however.

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The rapid extension of the possibilities provided by computing techniques suggest that in the near future it will be possible to calculate the electron affinity and ionisation potentials of chemical compounds of increasing complexity. Nevertheless, qualitative models which would make it possible to estimate these quantities without laborious calculations are of considerable interest. The analysis carried out in the present review has shown the existence of two important classes of chemical compound: with anomalously high EA (superhalogens) and with anomalously low first IP (superalkalies). Both classes of compound are of considerable interest for theoretical chemistry, since they extend the traditional concepts of the electronegativity and electropositivity of chemical groups. At the same time these compounds are important for practical purposes, for example for the synthesis of new chemical compounds and in the planned search for new dopants to increase the electrical conductivity of polymers, and also new counter-ions for the production of organic superconductors.

It is hoped that the above discussion of the electronic structure of superhalogens and superalkalies will attract the attention of experimental workers and find further theoretical development.

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The Reactions of Azoxybenzenes in Acids. The Mechanism of the Wallach Rearrangement

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Data concerning the use of various acids to effect the Wallach rearrangement in the series of azoxybenzenes are analysed and the influence of the chemical nature and position of the substituents on the reactions of azoxybenzenes in the presence of acids, including the Wallach rearrangement and side processes, are examined. Data obtained in the study of the mechanism of the Wallach rearrangement by kinetic and tracer atom methods are discussed and the effect of Lewis acids and UV radiation on azoxybenzenes is considered.

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I. INTRODUCTION

Organic compounds with a nitrogen-containing functional group play an exceptionally important role in natural and technological processes. Such compounds include medicinal preparations, dyes, pesticides, explosives, etc. The great theoretical and practical importance of these compounds has stimulated the study of the chemical properties of nitrogen-containing functional groups. Among organic nitrogen compounds, azoxybenzenes occupy a special place. As a result of their high thermal and chemical stabilities, all the compounds containing a nitrogen atom attached to the benzene ring can be ultimately converted into azoxybenzenes via oxidation or reduction regardless of the valence state of the nitrogen in the functional group (see, for example, Yandovskii et al.[1]).

On the other hand, the known instances of reversible reactions of azoxybenzenes are fairly few. This has aroused interest in the Wallach rearrangement, discovered more than one hundred years ago, which consists in the conversion of azoxybenzene into 4-hydroxy- and 2-hydroxy-azobenzenes on treatment with concentrated sulphuric acid. The availability of the starting materials and the simplicity of the conditions promoted the wide-scale employment and detailed study of the Wallach rearrangement, which is nowadays included among the principal synthetic methods of organic chemistry. The Wallach rearrangement has been investigated in special detail in relation to azoxybenzene itself: the fundamental features of its occurrence have been discovered and its mechanism has been seemingly elucidated. However, the data obtained in the studies during the last decade have shown that, even when the reaction conditions and the structures of the initial azoxybenzenes are altered only slightly, processes unrelated to the Wallach rearrangement proper begin to occur. Unusual reactions were then observed of the kind which it would perhaps be impossible to predict *a priori* at the present level of development of chemistry. It was also found that the mechanism of the rearrangement is more complex than appeared previously.

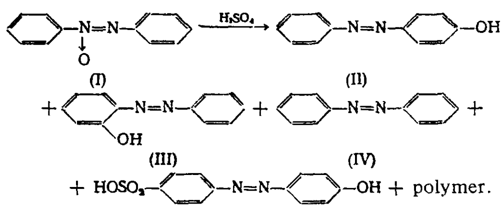
New data require the reconsideration of the accumulated results for a more adequate understanding of the situation which has arisen as regards the study and treatment of the Wallach rearrangement. Analysis of experimental data relevant to the Wallach rearrangement has been frequently carried out in a number of review articles and monographs and both individual aspects of this reaction and the reaction as a whole have been considered.[2-4] Japanese investigators, in Yamamoto's[5,6] and Oae's[7] schools, have made a major contribution to the discovery of the principal features of the Wallach rearrangement and the principal original studies in this field are due to these investigators. The fundamental investigations of Shemyakin's school, carried out by the tracer atom (^{15}N, ^{18}O) methods[8-10] have played a large role in the understanding of the mechanism of the rearrangement.[8-10] Data on the kinetics of the Wallach rearrangement have been obtained.[4,11]

Despite the large number of studies devoted to the mechanism of the Wallach rearrangement, a single view concerning the rearrangement has not so far been elaborated. One of the key questions, concerning the identification of the cationoid species responsible for the rearrangement, has remained unresolved. Olah et al.[12] put forward the hypothesis, shared by many chemists, that this species is a dication generated by the dehydrated diprotonated form of azoxybenzene. The data of the last few years, obtained in the study of the synthetic aspects of the Wallach rearrangement and its mechanism, are analysed in the present review. Earlier investigations are discussed only in those cases where this is required for the understanding of the new data.

II. THE INFLUENCE OF THE NATURE OF THE ACID AND THE ACIDITY FUNCTION OF THE MEDIUM ON THE ACID-CATALYSED REARRANGEMENT OF AZOXYBENZENES

In the course of the study of the behaviour of azoxybenzene in concentrated sulphuric acid, Wallach observed the formation of 4-hydroxyazobenzene together with 2-hydroxyazobenzene and other products (Scheme 1). Somewhat later, this result was confirmed by a number of workers who concluded that its character is general.[2,3]

Scheme 1



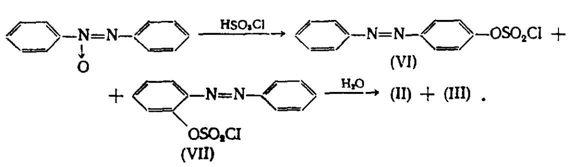
Kinetic data have shown that the rate of the rearrangement depends significantly on the acidity of the medium.[4] Thus, on passing from 75% ($-H_0 = 6.65$) to 99.99% ($-H_0 = 11.9$) sulphuric acid (at 25 °C), the rate constant increases by five orders of magnitude.

At the present time the range of acids used for the Wallach rearrangement is fairly large, starting with sulphuric acid ($-H_0 = 11.93$) and ending with the 1:1 HSO_3F-SbF_5 mixture ($-H_0 = 19.5$). There exist also individual examples of the employment of mixtures of acids (for example, toluene-*p*-sulphonic acid–acetic anhydride). However, these acid systems have no special advantages over sulphuric acid. Sulphuric acid (at a concentration >80%) is employed as a rule for the rearrangement. The product ratio (*ortho*:*para*) is 0.02%. It has been shown[13] that at these sulphuric acid concentrations the solvated proton H_3O^+ is not a sufficiently strong acid to catalyse the reaction considered. Stronger acids (H_2SO_4 and $H_3SO_4^+$) play the role of the catalyst under these conditions.

It has been suggested[11] that the product of the rearrangement of azoxybenzene in concentrated sulphuric acid is azobenzene-4-hydrogen sulphate, whose hydrolysis affords 4-hydroxyazobenzene. Indeed azobenzene-4-hydrogen sulphate hydrolyses in sulphuric acid with formation of 4-hydroxyazobenzene. It has been shown that under these conditions the nitrogen atom of the azo-group is initially protonated, which is followed by the slow protonation of the oxygen atom bound to the benzene ring, and finally the C–S bond is cleaved. The idea of the intermediate formation of 4-substituted esters with their subsequent hydrolysis to 4-hydroxyazobenzene was used to account for the processes occurring in different acids.[3,4]

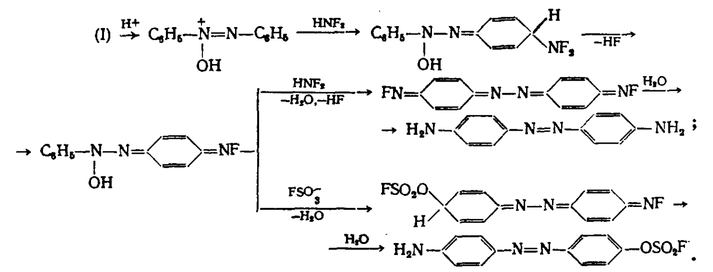
Dissolution of azoxybenzene in HSO_3Cl at −10 °C leads to the formation of its esters (VI) and (VII) (the *ortho*:*para* ratio is 0.51), which are readily hydrolysed by weak alkalis (Scheme 2):[14,15]

Scheme 2



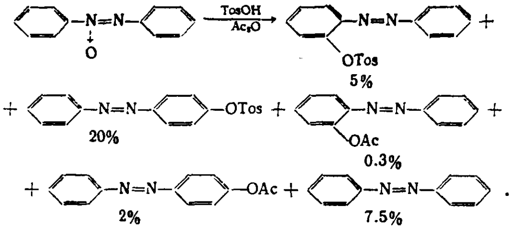
As in concentrated sulphuric acid, the rearrangement in HSO_3F leads to the preferential formation of the *para*-substituted product (II).[15,16]

The presence in the acid system of different anions, whose nucleophilicity has a decisive influence on the character of the products formed, is exceptionally important. For example, when the Wallach rearrangement is carried out in HSO_3F with added HNF_2, the products are 4-fluorosulphonyloxyazobenzene (17–35%), 4,4′-diaminoazobenzene (16–45%), and 4-amino-4′-fluorosulphonyloxyazobenzene (5–20%).[16] The amino-derivatives are formed via the intermediate fluoroimines:



When the Wallach rearrangement is performed in a mixture of acids containing different anions, different products are formed, for example both toluene-*p*-sulphonates and acetates are formed in the toluene-*p*-sulphonic acid–acetic anhydride mixture. This shows that in the second stage of the rearrangement the cationoid species generated from azoxybenzene interacts with the anion of the medium.[17] The *para*-substituted product predominates in this case too (Scheme 3).

Scheme 3



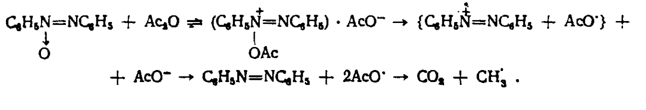
This demonstrates the important role of the second stage of the reaction, which consists in the attack by the nucleophile of the medium on the most electrophilic centre in the intermediate cationoid species responsible for the Wallach rearrangement.

When azoxybenzene is treated with 80% polyphosphoric acid, a mixture of 2-hydroxy- and 4-hydroxy-azobenzenes with an *ortho*:*para* ratio of 1.7 is formed (the yields of products are 26 and 11.8% respectively).[6] In addition 15.1% of azobenzene is produced.

When azoxybenzene is treated with toluene-*p*-sulphonic acid and polyphosphoric acid, azobenzene, the product of the reduction of azoxybenzene, is formed in appreciable amounts, which is extremely unexpected and difficult to explain. It has been shown[18] that azobenzene is the main product resulting from the treatment of azoxybenzene with the (1:1) ($HF-SbF_5$)–SO_2 mixture at −50 °C (yield 68–72%); the usual product of the Wallach rearrangement, namely 4-hydroxyazobenzene, is obtained in a yield less than 10%, while 2-hydroxyazobenzene is not detected at all. These data show that the nature of the acid used to effect the Wallach rearrangement influences not only the *ortho*:*para* ratio but also the course of the process itself, which is probably due to the difference in the reactivities of the species generated from azoxybenzene under the influence of different acids.

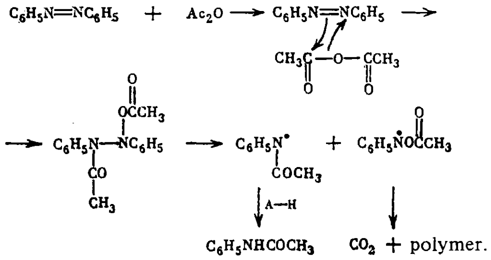
Azoxybenzene does not change in acetic acid at temperatures in the range 20–190 °C, while the addition of acetic anhydride leads to the formation of acetic acid and acetanilide in 70% yield (when the reactants are used in proportions of 1:5). On the other hand, for the equimolar reactant ratio, a complex mixture of products is formed in the system: azobenzene (60%), acetanilide (13%), acetic acid (63%), CO_2 (95%), CO (14%), and CH_4 (2%).[19] The authors suggest the following reaction mechanism (Scheme 4):

Scheme 4



$$C_6H_5\underset{\underset{O}{\downarrow}}{N}=NC_6H_5 + Ac_2O \rightleftharpoons (C_6H_5\underset{\underset{OAc}{|}}{\overset{+}{N}}=NC_6H_5)\cdot AcO^- \to \{C_6H_5\overset{+}{\dot{N}}=NC_6H_5 + AcO^\cdot\} + AcO^- \to C_6H_5N=NC_6H_5 + 2AcO^\cdot \to CO_2 + CH_3^\cdot\,.$$

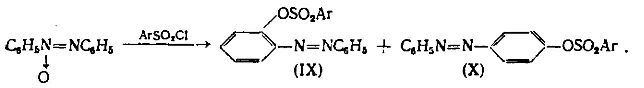
The acetanilide and CO_2 are obtained from azobenzene, which has been demonstrated independently by treating azobenzene with acetic anhydride. It has been suggested that the reaction proceeds as follows:



The usual products of the Wallach rearrangement, namely 2-hydroxy- and 4-hydroxy-azobenzenes, are formed from azoxybenzene in small yields in trichloroacetic acid in the presence of acetic anhydride.[20]

Thus the first feature of an acid system containing electrophilic CH_3CO^+ species is that reduction products and not the products of the Wallach rearrangements are formed, and the second feature is the possibility of catalysis of the Wallach rearrangement not only by H^+ but also by other cationoid species. The first stage under these conditions is attack by the cationoid species on the oxygen atom of the azoxy-group. Indeed, it has been found that, when azoxybenzene is heated with arenesulphonyl chlorides, the arenesulphonic esters (IX) and (X), the products of the Wallach rearrangement, are formed.[21] The *ortho* : *para* ratio then varies as a function of the nature of the arenesulphonyl chloride employed (Scheme 5):

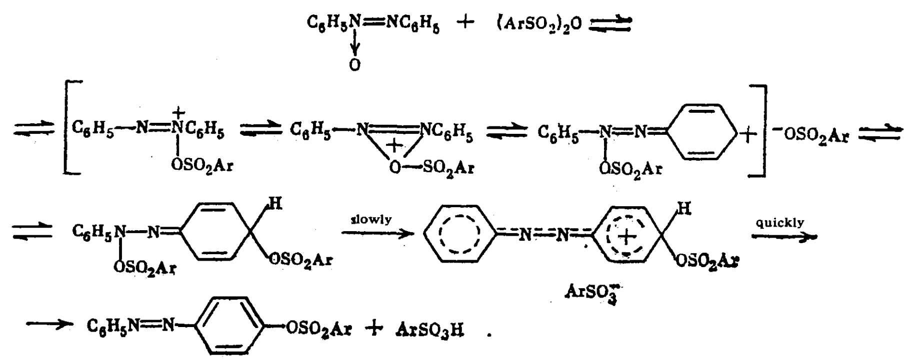
Scheme 5



Ar	(IX) Yield of (IX), %	(X) Yield of (X), %
$4\text{-}NO_2C_6N_4$	59.7	24.8
$4\text{-}BrC_6N_4$	28.8	36.8
$4\text{-}CH_3C_6N_4$	0.6	61.4
CH_3SO_2Cl	—	63.8

The rearrangement of azoxybenzenes proceeds also on treatment with the anhydrides of benzenesulphonic acids[22] (Table 1). However, the *para*-substituted product is formed exclusively in this case in high yields (Table 2). It has been suggested[22] that the reaction proceeds in accordance with Scheme 6.

Scheme 6

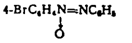
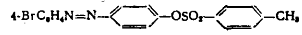
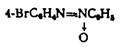
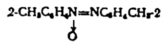
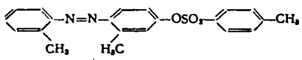
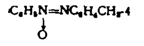
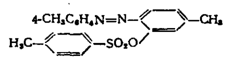
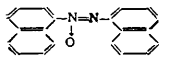
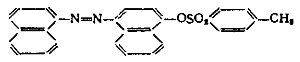


The kinetic data (in the presence of an excess of arenesulphonic acid anhydride, the reaction is of pseudo-first order, $E_a = 22.4$ kcal mol^{-1}, and $\Delta S^{\neq} = -14.2$ e.u.) and especially the influence of substituents both in the azoxybenzene ($\rho = -1.5$) and in the arenesulphonic acid anhydride ($\rho = +1.3$) on the rate of reaction show that the overall rate of this reaction is determined by the stage involving the cleavage of the N—C bond.[22]

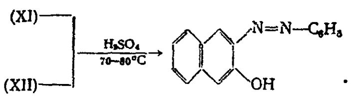
Table 1. The reactions of azoxybenzene with sulphonic acid anhydrides.[22]

Anhydride	Reaction product	Yield, %
Tos_2O	$4\text{-}TosOC_6H_4N{=}NC_6H_5$	92
$(C_6H_5SO_2)_2O$	$4\text{-}C_6H_5SO_2OC_6H_4N{=}NC_6H_5$	92
$(4\text{-}BrC_6H_4SO_2)_2O$	$4\text{-}(4\text{-}BrC_6H_4SO_2O)C_6H_4N{=}NC_6H_5$	86

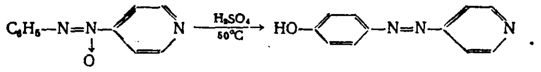
Table 2. The reactions of substituted azoxybenzenes with the anhydride of toluene-*p*-sulphonic acid.[22]

Compound	Product	Yield, %
 $4\text{-}BrC_6H_4\underset{\downarrow\atop O}{N}{=}NC_6H_5$		62
 $4\text{-}BrC_6H_4N{=}\underset{\downarrow\atop O}{N}C_6H_5$	ditto	75
 $2\text{-}CH_3C_6H_4\underset{\downarrow\atop O}{N}{=}NC_6H_4CH_3\text{-}2$		74
 $C_6H_5\underset{\downarrow\atop O}{N}{=}NC_6H_4CH_3\text{-}4$		68
		70

Like azoxybenzene, azoxy-compounds of the naphthalene series undergo the Wallach rearrangement.[23,24] It has been shown that, when 2-naphthyl-*ONN*-azoxybenzene (XI), 2-naphthyl-*NNO*-azoxybenzene (XII), 1,1′-azoxynaphthalene, 1,2′-*ONN*-azoxynaphthalene, and 2,2′-azoxynaphthalene are treated with sulphuric acid (at a concentration in the range 60—93%), the Wallach rearrangement is observed and the corresponding hydroxyazo-derivatives are formed, the site of attack by the nucleophile being the *ortho*-position in the naphthalene nucleus:



On the other hand, the introduction of the dimethylamino-group into the benzene ring, for example in the case of 2-naphthyl-*ONN*-azoxy(4′-dimethylaminobenzene), prevents the Wallach rearrangement in 70% sulphuric acid (as a result of the protonation of its nitrogen atom).[25] However, at a sulphuric acid concentration of 97—99.9% protonation at the substituent does not prevent the rearrangement.[26] Thus 4-pyridyl-*NNO*-azoxybenzene affords under these conditions 4-(4′-hydroxyphenylazo)-pyridine. However, 4-pyridyl-*ONN*-azoxybenzene does not rearrange under these conditions, which indicates the importance also of the very structure of the azoxy-derivative for the acid-catalysed rearrangement:



Analogous characteristics have been discovered also for the isomeric (α- and β-) 4-(phenylazoxy)pyridine *N*-oxides.[27] Kinetic data for the rearrangement of 4-pyridyl-*NNO*-azoxybenzene have shown that, on passing from 98.46% to 99.91% sulphuric acid, the rate constant increases by two orders of magnitude.[26]

Thus the character of the acid employed has a significant influence on the products of the Wallach rearrangement.

III. THE INFLUENCE OF SUBSTITUENTS ON THE WALLACH REARRANGEMENT

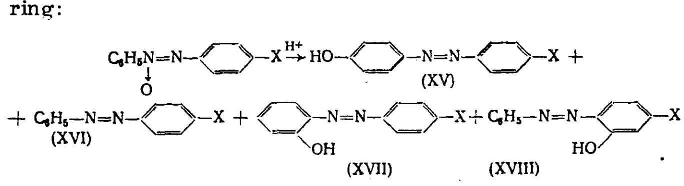
The introduction of electron-accepting substituents in the azoxybenzene molecule reduces the electron-donating capacity of the oxygen atom of the azoxy-group and increases the electron-accepting capacity of the carbon atoms in the benzene rings (Table 3).[28]

Table 3. The basicities of 4-substituted *NNO*-azoxybenzenes.[28]

X	pK_a	X	pK_a
OCH_3	-6.10 ± 0.04	H	-6.45 ± 0.05
OC_2H_5	-6.04 ± 0.03	Br	-7.01 ± 0.04
CH_3	-6.04 ± 0.03	NO_2	-9.83 ± 0.07

For this reason, substituents influence both the rate of the Wallach rearrangement and the nature of the products, so that the study of the influence of the chemical nature and position of the substituent in azoxybenzene on the reactivity and the type of products under the conditions of the Wallach rearrangement is extremely important for the question under consideration. In particular, this applies to those cases where structural factors hinder the Wallach rearrangement and the character of the acid system can promote other processes. Indeed, it will be seen from the data presented below that in many instances unexpected products are formed, which can be explained both from the standpoint of the stabilising influence of the substituent on the cationoid species and on the basis of the character of the electrophilic intermediate generated.

We shall consider in the first place the influence of the halogen in the 2- and 4-positions on the Wallach rearrangement. When 4-halogenoazobenzenes are treated with sulphuric acid, the main products are 4-halogeno-4-hydroxyazobenzenes, i.e. the OH group is in the unsubstituted benzene ring:



The ratio of the products varies little as a function of the structure of 4-halogenoazoxybenzene, i.e. as a function of whether it is the α- or β-isomer [4-halogeno-*ONN*-azoxybenzene (XIII) or 4-halogeno-*NNO*-azoxybenzene (XIV)] (Table 4).[29]

Table 4. The reactions of 4-halogeno-*ONN*-azoxybenzenes with sulphuric acid (92%, 50 °C, 30 min).[29]

X	Yield, %			
	(XV)	(XVI)	(XVII)	(XVIII)
F	54	26	0.5	0.3
Cl	34	46	1.4	0.2
Br	27	55	1.7	0.3
I	5	72	2.0	0.3
Br*	27	52	2.0	0.1

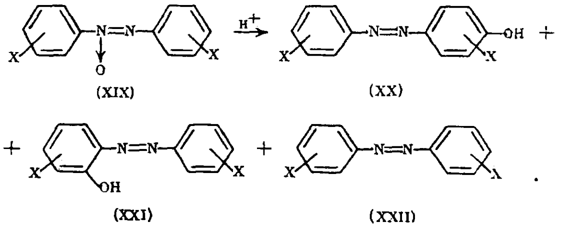
*The β-isomer.

Table 5. The reactions of azoxybenzenes with acids.

X	Reagent*	Amount of product (XIX) recovered, %	Yield, %			Refs.
			(XX)	(XXI)	(XXII)	
2,2′-Br_2	H_2SO_4 (82%)	14.1	62.7	—	33.8	[6]
2,2′-Br_2	HSO_3Cl	41.5	33.4	2.4	20.9	[6]
2,2′-Br_2	H_2PO_4 (80%)	74.3	3.9	3.9	—	[6]
2,2′-Cl_2	H_2SO_4 (82%)	16.2	75.3	—	15.7	[6]
2,2′-Cl_2	HSO_3Cl	51.4	30.5	—	23.7	[6]
2,2′-Cl_2	H_3PO_4 (80%)	68.5	3.2	3.2	5.4	[6]
3,3′-Cl_2	H_2SO_4 (92%)	75	16	1	—	[30]
4,4′-Cl_2	H_2SO_4 (92%)	—	—	13	58	[30]
4,4′-Br_2	H_2SO_4 (92%)	—	—	15	59	[30]
2-Cl	H_2SO_4 (78%)	13.6	35.4	6.9	30.3	[31]
2,2′-Cl_2	H_2SO_4 (78%)	28.4	43.5	0	11.8	[31]
4,4′-Cl_2	H_2SO_4 (78%)	71.6	—	7.3	18.1	[31]
2,2′,4,4′-Cl_4	H_2SO_4 (78%)	73.5	0	0.5	17.1	[31]

*The concentration is given in brackets.

In the case of azoxybenzenes where the halogen atoms are in the 2,2′- and 3,3′-positions, treatment with different acids leads to the products of the Wallach rearrangement (4-hydroxydihalogenoazobenzenes) together with appreciable amounts of the corresponding dihalogenoazobenzenes (Table 5):



The Wallach rearrangement takes place selectively in the *para*-position. However, when both *para*-positions in the benzene ring are occupied, it takes place in the *ortho*-position. At the same time detailed study of the products of the reaction of 4,4'-dihalogenoazoxybenzenes in 92% sulphuric acid revealed a number of unexpected substances, among which compounds (XXV), (XXVI), and (XXVIII) were found.[28] The yields of the products are presented in Table 6.

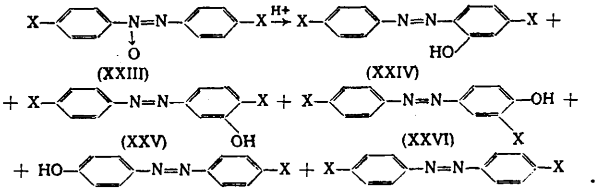
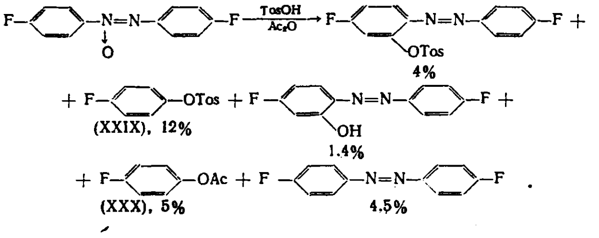


Table 6. The reactions of 4,4'-dihalogenoazoxybenzenes (XXIII) with 92% sulphuric acid (50 °C, 30 min).[29]

X	Composition of reaction mixture, %				
	(XXIV)	(XXV)	(XXVI)	(XXVII)	(XXVIII)
F	0.6	7.4	—	25	40
Cl	12	3.6	2.4	0.2	59
Br	11	—	1.5	0.2	69
I	1	—	—	—	83

The pathways leading to their formation will be examined below. The data in Table 6 illustrate the influence of the nature of the halogen on the character of the products of the reactions of azoxybenzenes in sulphuric acid. In all cases, azobenzenes are formed in appreciable amounts and, when X = F or I, compounds of type (XXVI) are absent from the products. In the case of 4,4'-difluoroazoxybenzene, the influence of the acidity of the medium on the ratio of the reaction products was also observed. Thus, on passing from 85% to 98% sulphuric acid, the yield of the products (XXV) and (XXVIII) increases and the yield of compound (XXVII) falls sharply. Treatment of 4,4'-difluoroazoxybenzene with toluene-*p*-sulphonic acid in the presence of acetic anhydride leads to the products (XXIX) and (XXX) as a result of the interaction of the anions of the medium with the 4-fluorophenyl cation.[17] This presupposes the cleavage of the C–N bond in the protonated form of 4,4'-difluoroazoxybenzene and the subsequent conversion of the 4-fluorobenzenediazonium cation into the 4-fluorophenyl cation:

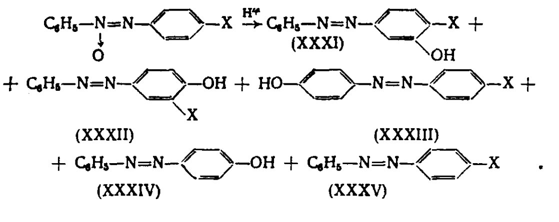


Naturally the formation of these products and their reactions do not take place in the same way in different media. Treatment of 4,4'-dichloroazoxybenzene with the TosOH–Ac_2O acid system at 100 °C leads to a complex mixture of products: 2-tosyloxy-4,4'-dichloroazoxybenzene (3%), 4,4'-dichloroazobenzene (5.5%), 4-chlorophenyl toluene-*p*-sulphonate (0.5%), and 4,4'-dichloro-2'-hydroxyazobenzene (0.5%).

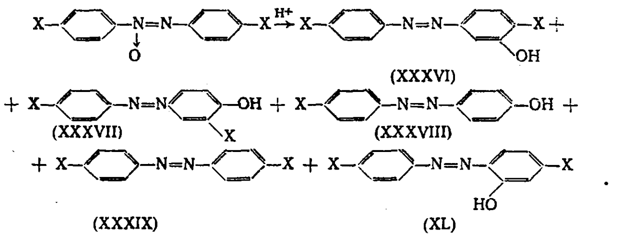
The accumulation of halogen atoms in the benzene ring tends to increase the content of azobenzenes. Thus 59% of 4,4'-dichloroazobenzene is formed from 4,4'-dichloroazoxybenzene in 90% sulphuric acid, while 2,2',4,4'-tetrachloroazoxybenzene gives rise to 76.8% of 2,2',4,4'-tetrachloroazobenzene. The exclusive formation of the products of the reduction of 2,2',4,4'-tetrachloroazoxybenzene is observed also in other acids—chlorosulphonic acid and 80% polyphosphoric acid.[31] However, account must be taken of the role of the nature of the acid in the overall set of reactions of azoxybenzene in acid media. Thus it has been shown[32] that 2,2',3,3',5,5',6,6'-octafluoroazoxybenzene does not undergo the Wallach rearrangement on treatment with HSO_3F, HF, and H_2SO_4, whereas the formation of the products of this rearrangement, namely 4-chlorosulphonyloxy-2,2',3,3',5,5',6,6'-octafluoroazobenzene, is observed in HSO_3Cl, although it is slow. On the other hand, treatment with the very strong 1 : 1 HSO_3F–SbF_5 acid mixture at 20 °C leads to the formation of only 2,2',3,3',5,5',6,6'-octafluoroazobenzene after hydrolysis. We may note that azoxybenzenes for which the Wallach rearrangement is impossible, for example, decafluoroazoxybenzene and 4,4'-dimethyloctafluoroazoxybenzene, give rise to decafluoroazobenzene and 4,4'-dimethyloctafluoroazobenzene respectively in this acid system.

Thus the data presented indicates the importance for the Wallach rearrangement of factors such as the position of the substituent in the benzene ring, the nature of the acid, the presence of active nucleophiles in the system, and the reaction conditions. It is therefore natural to expect that the same features as for the halogeno-substituents will be observed also for other substituents, such as the alkyl, alkoxy-, nitro-, carboxy-, etc. groups.

Indeed, treatment of 4-alkylazoxybenzene with sulphuric acid leads to the formation of both the usual products of the Wallach rearrangement (XXXIII) and the "anomalous" compounds (XXXI), (XXXII), and (XXXIV)[33] and their ratio varies with the character of the alkyl substituent. Thus compound (XXXI) predominates for the CH_3 substituent, whereas compound (XXXIV) is formed exclusively for $CH(CH_3)_2$ and $C(CH_3)_3$. This may be associated with the ability of the group X to be split off in the form of the cationoid species from the product of the addition of the anion in the second stage of the Wallach rearrangement:



The formation of "anomalous" products was to be expected also for 4,4'-dialkylazoxybenzenes. In fact, when such azoxybenzenes are treated with sulphuric acid, compounds (XXXVI), (XXXVII), and (XXXVIII) are formed together with the azo-compounds (XXXIX) and the 2-hydroxyazo-compounds (XL).[30] However, the ratios of these products depend significantly on the character of the alkyl substituents. Thus, on passing from CH_3 to the $C(CH_3)_3$ group, the yield of 4,4'-dialkylazobenzenes increases by a factor of 2 and that of compounds of type (XXXVIII) by a factor of 51. On the other hand, compounds (XXXVI) and (XXXVII) are obtained only in trace amounts from azoxybenzenes containing the $CH(CH_3)_2$ and $C(CH_3)_3$ groups. These features can be explained by the ability of the alkyl group to form stable carbonium ions:

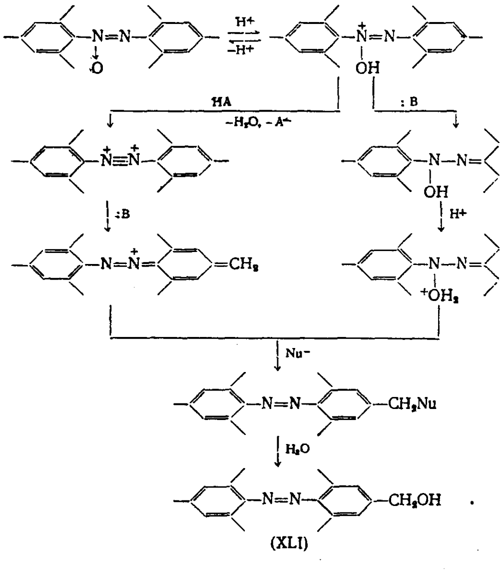


The features which can be accounted for by the ability of the alkyl group to form stable carbonium ions are also manifested here.

The use of a softer acid (trichloroacetic acid), which is used together with acetic anhydride, leads to the formation of the normal products of the Wallach rearrangement from 2,2′-dimethyl- and 4,4′-dimethyl-azoxybenzenes, namely 4-hydroxy- and 2-hydroxy-azobenzenes, in good yields.[5]

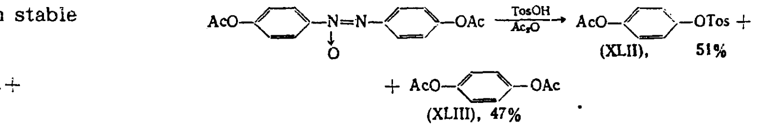
2,2′,4,4′,6,6′-Hexamethylazoxybenzene, for which the Wallach rearrangement is impossible, rearranges in a different way on treatment with concentrated sulphuric acid, i.e. the OH group is now located at the carbon atom of the methyl group in the *para*-position and 4-(hydroxymethyl)-2,2′,4′,6,6′-pentamethylazobenzene (XLI) is formed (in 91.5% yield in 85.6% sulphuric acid.[34–36] It has been suggested that the rearrangement proceeds in this case in accordance with Scheme 7.

Scheme 7



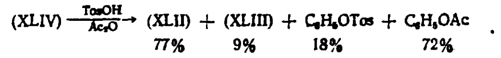
(XLI)

It has been found[37] that the reaction of 4,4′-dimethoxyazoxybenzene with the toluene-*p*-sulphonic acid—acetic anhydride mixture at 100 °C affords 3-acetoxy-4,4′-dimethoxyazobenzene (42%), 4,4′-dimethoxy-2-tosyloxyazobenzene (3.5%), and 4,4′-dimethoxyazobenzene (32%). 4-Methoxyazoxybenzene produces 3-acetoxy-4-methoxyazobenzene (38%), 4-methoxy-4′-tosyloxyazobenzene (5.6%), and 4-methoxyazobenzene (42%) in this acid system together with a small amount of the products of the hydrolysis of the esters, for example, 3-hydroxy-4-methoxyazobenzene.[37] Furthermore, the dissolution of 4,4′-diacetoxyazoxybenzene in the same acid system altogether fails to give rise to the product of the Wallach rearrangement and the exclusive formation of the products of 1-*unco*-substitution and the evolution of nitrogen are observed:[17]



Similarly, 2,2′-diacetoxyazoxybenzene gives rise to 2-acetoxyphenyl toluene-*p*-sulphonate (41%), 1,2-phenylene diacetate (18%), and 2,2′-diacetoxy-4-tosyloxyazobenzene (16%). We may note that, in the case where the anhydride of toluene-*p*-sulphonic acid in acetonitrile is used, refluxing for 2 h produces compound (XLII) in 16% yield, while in sulphuric acid in the presence of acetic anhydride at 100 °C, compound (XLIII) is formed after 1 h (yield 35%).

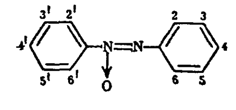
4-Acetoxy-*ONN*-azoxybenzene and 4-acetoxy-*NNO*-azoxybenzene (XLIV) behave in the same way in acetic anhydride (100 °C, 2 h) as in TosOH, the only difference between them being that the β-isomer reacts more slowly:[17]



$$(\mathrm{XLIV}) \xrightarrow[\mathrm{Ac_2O}]{\mathrm{TosOH}} \underset{77\%}{(\mathrm{XLII})} + \underset{9\%}{(\mathrm{XLIII})} + \underset{18\%}{C_6H_5OTos} + \underset{72\%}{C_6H_5OAc}\ .$$

The behaviour in acids of azoxybenzenes containing electron-accepting substituents in the 4,4′-positions differs from that examined above. Thus treatment of 4,4′-dinitro- and 4,4′-dicarboxy-azoxybenzenes with concentrated sulphuric acid yields the products of the Wallach rearrangement—the corresponding 2-hydroxyazobenzenes.[37] 4,4′-Dinitro-4,4′-dicarboxy-azobenzenes are formed in very low yields. On the other hand, the presence of the CH_3CO group results in the formation of an azo-compound in which the CH_3CO group has been replaced by the OH group.

Table 7. Kinetics of the reaction of azoxybenzene with sulphuric acid (at 30 °C).[42]



X	$10^7 k$, s^{-1}			pK_a
	$[H_2SO_4]$ = 83.6%	$[H_2SO_4]$ = 90%	$[H_2SO_4]$ = 98%	
3,3′-$(NO_2)_2$	—	0.25	18	—8.01
4-NO_2	—	3.5	320	—6.18
3-NO_2	0.28	6.5	684	—6.33
4′-NO_2	—	300	33 300	—6,21
3′-NO_2	9	450	38 000	—6.47
H	200	1 280	9 170	—5.13
3,3′-$(OCH_3)_2$	110	1 350	—	—5.15
4-Br	467	2 920	—	—5.03
4-OH	6120	33 000	—	—5.21

The presence of the NO_2 group in only one benzene ring (the α- and β-isomers) leads to the rearrangement product in which the OH group is in the other benzene ring. Thus 4-hydroxy-4′-nitroazobenzene is formed in 83% yield in 92% sulphuric acid.[6,38] When HSO_3Cl is used, a mixture of products is formed from the α- and β-isomeric 4-nitroazoxybenzenes: 4-hydroxy-4′-nitroazobenzene, 2-hydroxy-4′-nitroazobenzene, and 4-nitroazobenzene.[39] Comparison of these data with the results obtained in concentrated sulphuric acid shows an increase of the *ortho* : *para* ratio for HSO_3Cl.[39]

The presence of a substituent in the 4-position, for example, CH_3CO,[33] AcNH, CH_3COO, and $(CH_3)_2N \rightarrow O$[40] prevents the Wallach rearrangement. Thus azoxybenzene with the $(CH_3)_2N \rightarrow O$ substituent gives rise to a 55.1% yield of

4-hydroxy-4′-dimethylaminoazobenzene in 100% sulphuric acid, which is the first example of the involvement of tertiary amine *N*-oxides in the Wallach rearrangement. If the reactant ratio is 1 : 1, the overall yield of 2-hydroxy- and 4-hydroxy-4′-dimethylaminoazobenzenes is ~22%, and for the 4 : 1 ratio, where there is a significant deficiency of acid, the Wallach rearrangement does not take place. In this case the tertiary amine *N*-oxide is reduced with formation of a mixture of α- and β-isomers of 4-dimethylamino-*ONN*-azoxybenzene. A similar reaction in an acid medium has been observed also for *N*-pentafluorophenylpiperidine oxide.[41]

Kinetic data for the influence of the nature and position of the substituent in the benzene ring on the rate of rearrangement indicate its dependence on the acidity function of the medium and the pK_a of the initial azoxybenzene (Table 7).[42]

The electron-accepting properties of the substituent in the 4-position in the benzene ring apparently exert an appreciable influence on the rate of the Wallach rearrangement. According to the results of kinetic studies, the rate of rearrangement is proportion to $[H^+]^2$.[4] Because of this, the presence of an electron-donating group, whose heteroatom is capable of interacting with the proton should lower the rate of rearrangement and should lead to the necessity for the employment of a stronger acid system. Indeed, it has been shown[25] that 4-dimethylamino-1-naphthyl-*ONN*-azoxybenzene does not undergo the Wallach rearrangement in 70% sulphuric acid; only protonation at the dimethylamino-group takes place under these conditions.

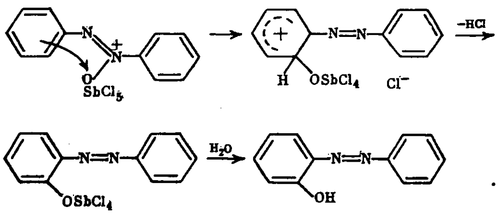
IV. THE EFFECT OF LEWIS ACIDS ON AZOXYBENZENES

The study of the reactions of azoxybenzenes with Lewis acids showed that 1 : 1 complexes are formed initially, giving rise to azobenzene as the main product on heating. Thus treatment of azoxybenzene with PCl_3 produces a 95% yield of azobenzene.[43] On the other hand, $AlCl_3$ and $FeCl_3$ afford 4-chloroazobenzene in yields of 83 and 63% respectively. If the reaction of $AlCl_3$ is carried out in SO_2Cl_2, then 4,4′-dichloroazobenzene is obtained in 70% yield, while in $SOCl_2$ a mixture of products is formed: 4-chloroazobenzene (3.1%), 4,4′-dichloroazobenzene (5.2%), and azobenzene (75.3%).[43] The reaction in nitromethane gives rise to 65% of 4-chloroazobenzene, 4% of 4,4′-dichloroazobenzene, 6% of 2-chloroazobenzene, 18% of 2,4-dichloroazobenzene, and 48% of 2,4′-dichloroazobenzene.[44]

When the reaction of azoxybenzene with $ZnBr_2$, $FeCl_3$, $AlCl_3$, and $TiCl_4$ is carried out in nitromethane, refluxing affords azobenzene as the main product and its amount increases with increase of the strength of the Lewis acid, the products of the Wallach rearrangement being obtained in trace amounts.[45]

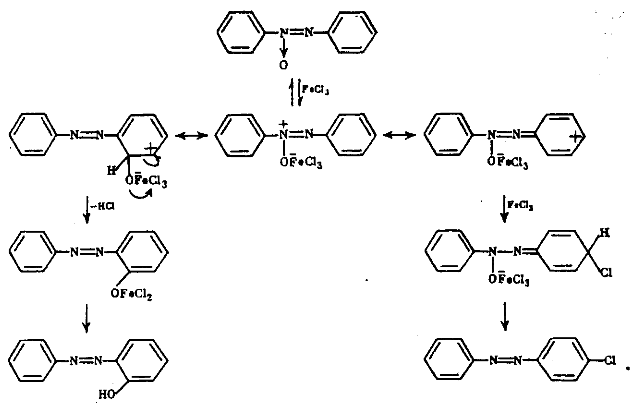
The structure of the reaction products can be influenced decisively by coordination. Thus thermolysis of the complexes of azoxybenzene with $SbCl_5$ leads selectively to an *ortho*-substituted product of the Wallach rearrangement.[45–47] It has been suggested that the reaction proceeds in accordance with Scheme 8:

Scheme 8



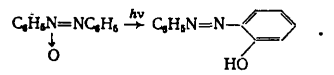
The reactions of substituted azoxybenzenes with $FeCl_3$ [48] or $AlCl_3$ [49] lead exclusively to the formation of reduction products—substituted azobenzenes. 4′-Chloro-2-hydroxyazobenzene and 4-chloroazobenzene have been obtained in proportions of ~1 : 1 only from 4-chloro-*NNO*-azoxybenzene (β-isomer). The formation of the corresponding chloro-derivatives of azobenzenes is striking and can be accounted for in terms of Scheme 9:

Scheme 9



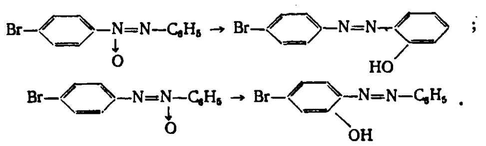
V. THE PHOTO- AND THERMO-INITIATED WALLACH REARRANGEMENT

In 1925 Cumming observed that irradiation of a solution of azoxybenzene in ethanol with UV light from a mercury lamp leads to the formation of 2-hydroxyazobenzene:

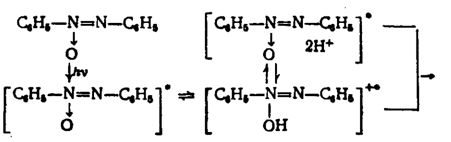


28%

It has been shown[48] that, on exposure of solutions of a number of asymmetrically substituted azoxybenzenes and benzene to sunlight, the oxygen atom of the azoxy-group is transferred to the benzene ring linked to the −N= fragment of the azoxy-group. Since the −N= valence angle is 120°, the oxygen atom is closest to the *ortho*-position of the neighbouring ring. For example, in the rearrangement of α- and β-isomeric 4-bromo-*NNO*-azoxybenzenes, the hydroxy-group is transferred to the benzene ring which in the initial compound was not bound to the NO fragment:



These facts lead to the conclusion that the photoinitiated Wallach rearrangement is intramolecular in character. It has been postulated[49] that it proceeds as follows:

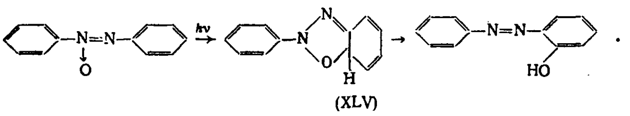


(III) .

With the aid of azoxybenzene labelled with ^{15}N at the site of the nitrogen atom of the azoxy-group not linked to the oxygen atom, it has been shown[9] that the equalisation of the isotope composition of the nitrogen is not observed for 2-hydroxyazobenzene and the labelled atom is in the benzene ring containing the hydroxy-group. With the aid of ^{18}O-labelled azoxybenzene, it has been demonstrated[8] that the isotope composition of the oxygen of the hydroxy-group in the 2-hydroxyazobenzene produced does not differ from that of the oxygen of the azoxy-group of the initial azoxybenzene. Consequently, in this rearrangement the hydroxy-group of 2-hydroxyazobenzene is formed from the oxygen of the azoxy-group and the reaction is intramolecular. Hence one may conclude that the rearrangement of azoxybenzene to 2-hydroxyazobenzene bypasses the symmetrisation stage and the benzene ring remote from the $=\underset{\downarrow \atop O}{N}-$ group is hydroxylated.

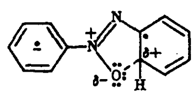
On the other hand, when [1-^{14}C]azoxybenzene in ethanol is irradiated, the distribution of the ^{14}C isotope label in the reaction products is inconsistent with an intramolecular rearrangement alone.[21] Thus the specific radioactivity of ^{14}C in the rearranged product is below that of the starting material.[21] This presupposes the simultaneous occurrence of α—β isomerisation and has been indicated also by the results of another study[50] where it was shown that irradiation of α- and β-4-methoxyazoxybenzenes in sulphuric acid results in the formation of 2-hydroxy-4-methoxyazobenzene. The rates of the Wallach rearrangement and α—β isomerisation depend on the character of the substituents in the benzene ring.

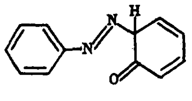
The photochemical reactions of 2,2′,6,6′-tetramethyl- and 2,6-dimethyl-*NNO*-azoxybenzenes have been studied in detail;[51] it has been concluded that the nucleophilic attack by the O atom of the azoxy-group on the benzene ring with the intermediate formation of compound (XLV) is more likely than the homolytic abstraction of an H atom from the *ortho*-position with subsequent transfer of the OH group. This conclusion has been confirmed by measurements of the quantum yields of the photochemical reaction and by the study of the isotope effect in the photoisomerisation of [D_{10}]azoxybenzene. The rate-limiting stage of the photochemical reaction of azoxy-compounds is probably the intramolecular migration of an H atom and not the formation of compound (XLV):



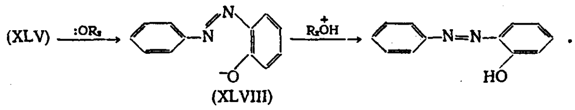
The nature of the substituent and its position in the benzene ring influence significantly the quantum yield of the photochemical reaction of substituted azoxybenzene. Thus the quantum yields in the rearrangements of 4-methyl- and 4-trifluoromethyl-*NNO*-azoxybenzenes are 0.37 and 1.70, while the corresponding yields for 3,5-dimethyl- and 3,5-bis(trifluoromethyl)-*NNO*-azoxybenzenes are 0.80 and 2.5 respectively.[52]

In their discussion of the pathways leading to the formation of compound (XLV), the authors[52] begin with the hypothesis that, on π,π* excitation of azoxybenzene, the less stable singlet state is converted into the more stable triplet state (XLVI) as a result of the interaction in the electronically excited state of the electrophilic oxygen radical and the electron-enriched remote benzene ring.


(XLVI)

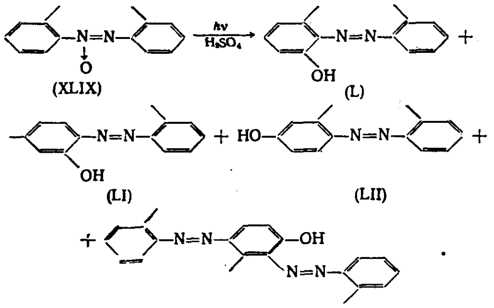

(XLVII)

In the presence of moderately basic solvents, for example, ethanol or diethyl ether, compound (XLV) is converted into the reaction product (III) via the anion (XLVIII):



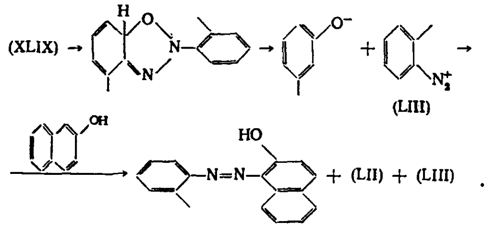
The formation of side products of the photochemical reaction has been attributed to the intermediate (XLVII) obtained from compound (XLV) by the intramolecular hydride 1,2-shift. A diazonium ion is formed from compound (XLVII), having been detected by the coupling reaction with β-naphthol.[52] Naturally, the above discussion is general so that one cannot claim to be able to explain many details of the process.

Interesting data have been obtained in the study of the photochemical reaction of 2,2′-dimethylazoxybenzene (XLIX)[53] in which unexpected products are formed:



The authors demonstrated (by adding β-naphthol to the system) the involvement of the arenediazonium cation (LIII) in this reaction (Scheme 10):

Scheme 10



It has been demonstrated[54] that, when 4- and 4′-substituted methoxy- and dimethylamino-derivatives of azoxybenzene are irradiated, 2- and 2′-hydroxyazobenzenes are formed. The authors suggest that the reaction proceeds via the intermediate formation of compounds of type (XLV).

If azoxybenzene is heated to 250 °C, its exothermic decomposition takes place and tarry substances are obtained together with azobenzene; 4-hydroxy- and 2-hydroxy-azobenzenes are formed in insignificant amounts.[55] The thermal reactions of azoxybenzenes have been investigated in detail.[56]

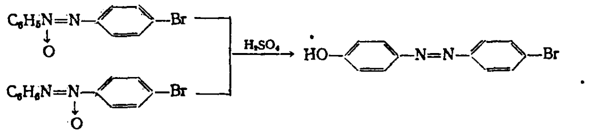
VI. THE MECHANISM OF THE WALLACH REARRANGEMENT

Up to the 1960's, the studies on the Wallach rearrangement were concentrated mainly on its synthetic aspects and virtually no attention was devoted to the mechanism of this reaction. The hypotheses put forward concerning the mechanism of the Wallach rearrangement were speculative and were not supported by experimental data. Only after the fundamental investigations of Shemyakin's school[8–10] and Buncel's kinetic measurements[4] were the first well-founded ideas concerning the mechanism of the Wallach rearrangement formulated. However, despite the large number of publications on this topic, after the above studies no serious step of any kind was taken towards the understanding of the mechanism of the Wallach rearrangement. On the contrary, a number of experimental data which could not be explained were published. The complexity of the study of the Wallach rearrangement was caused primarily by the possibility of the formation of a multiplicity of intermediates on dissolution of azoxybenzene in acid, each of which can influence the subsequent course of the reaction. The question of which cationoid species determines the rate of the Wallach rearrangement remains unresolved.

In the study of certain acid-catalysed rearrangements, for example the rearrangements of diazoaminobenzenes to phenylhydroxylamines, it was concluded that the mode of substitution in the benzene ring can be used to achieve the understanding of their mechanism. Thus mainly the *para*-substituted products should be formed via the intermolecular mechanism while the intramolecular mechanism gives rise mainly to *ortho*-substituted products. In those cases where 4-hydroxyazobenzenes are formed exclusively from azoxybenzenes, an intermolecular mechanism of the Wallach rearrangement might have been postulated. We shall deal with certain aspects of the mechanism of the Wallach rearrangement.

1. Acid-Catalysed α-β Isomerisation of Azoxybenzenes

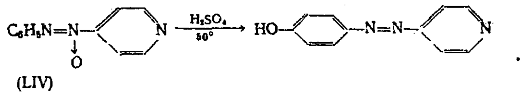
Both the α- and β-isomers of 4-bromoazoxybenzenes undergo an acid-catalysed rearrangement and the same product is formed: 4-bromo-4′-hydroxyazobenzene. Thus the hydroxy-group is in both cases in the *para*-position relative to the unsubstituted benzene ring:



This has also been observed for the α- and β-isomers of 4-methoxyazoxybenzenes. On the other hand, it has been unexpectedly observed that the main product of the reactions of the α- and β-isomers of 4-methylazoxybenzenes corresponds to the migration of the oxygen atom to the *ortho*-position in the unsubstituted benzene ring.[57] In a later study[58] it was shown that the α- and β-isomers of 4-methylazoxybenzene in 80–90% sulphuric acid form only 2-hydroxy-4-methylazobenzene, while the α- and β-isomers of 4-nitroazoxybenzene afford 4-hydroxy-4′-nitroazobenzene. 4-Bromo-*ONN*-azoxybenzene does not undergo the Wallach rearrangement, while 4-bromo-*NNO*-azoxybenzene gives rise to 4-bromo-2-hydroxyazobenzene under these conditions.

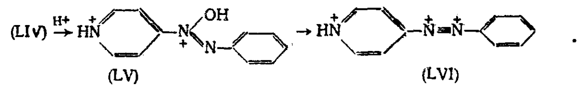
It has been found that the rates of rearrangement of the isomers are different and depend on the character of the substituent in the benzene ring. The use of identical conditions for the rearrangement of the α- and β-isomeric azoxybenzenes showed that the rate of rearrangement of α-isomers is higher for the CH_3 substituent and lower for the NO_2 and Br substituents. The ratio of the rates of rearrangement of α- and β-isomeric azoxybenzenes depends also on the acidity of the medium employed.

An example of an extremely large difference between the rates of rearrangement of the α- and β-isomers has been observed[26] for 4-[benzene-α(β)-azoxy]pyridines (LIV):



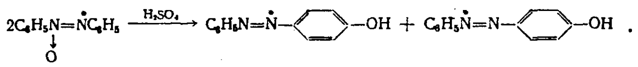
(LIV)

In this case only the β-isomer (LIV) undergoes rearrangement, while the α-isomer remains unchanged, which has been used to isolate it in a pure state. Kinetic measurements showed that the formation of the intermediate species (LVI) (the triprotonated form), as a result of the protonation of the nitrogen atom of the pyridine ring and the azoxy-group, is the rate-determining stage of the reaction:



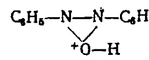
(LV) (LVI)

Whether or not the α–β isomerisation is intramolecular can be elucidated by studying the behaviour in acids of azoxybenzenes labelled at one of the nitrogen or carbon atoms by the ^{15}N or ^{14}C isotopes. These data can also provide an answer to the question which of the benzene rings does the hydroxy-group enter in the Wallach rearrangement. Shemyakin et al.[9] used azoxybenzene labelled with the ^{15}N isotope at one of the nitrogen atoms of the azoxy-group. They found that the formation of 4-azoxyazobenzene is accompanied by the complete equalisation of the isotope compositions of the nitrogen in both positions and they concluded that both benzene rings are hydroxylated to the same extent:



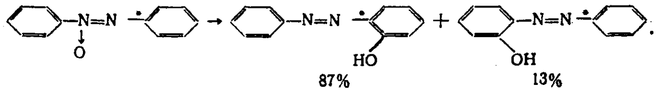
It has been established[9] that the observed equalisation of the distribution of the isotope label takes place during the period of the Wallach rearrangement itself and not before it. It has been demonstrated that the rearrangement of azoxybenzenes is not preceded by reversible isomerisation and that the rearrangement is not coupled with the preliminary conversion of the azoxybenzene to azobenzene, which is then hydroxylated.

The equalisation of the isotope compositions of the nitrogen in the final rearrangement product can indicate that the α–β isomerisation proceeds via a stage involving the formation of a free cation, which exists independently. Shemyakin et al.[9] suggested that this can be the oxonium cation (LVII), which is in fact responsible for the Wallach rearrangement.



(LVII)

These conclusions received some confirmation in a study[59] whose authors used azoxybenzene labelled with ^{14}C at the carbon atom linked to the nitrogen atom of the azoxy-group:



However, the ratio of the products formed is 87 : 13, which throws doubt on the necessity for the intermediate formation of the oxonium cation and its role in the mechanism of the Wallach rearrangement, confirming the possibility of the isomerisation of azoxybenzenes in an acid medium via the corresponding intermediate. Later these results were confirmed on the same object by other workers.[58] There is now no doubt that the acid catalysed α–β isomerisation is a general property of azoxybenzenes and proceeds independently of the Wallach rearrangement. It may be that this isomerisation takes place via the species (LVII).

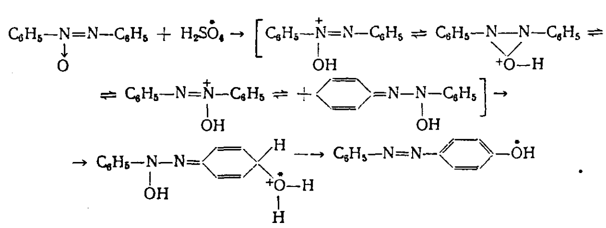
2. Data Obtained By the Tracer Atom (^{15}N, ^{18}O, ^{14}C) Method

An important factor in the understanding of the mechanism of the Wallach rearrangement was the solution of the problem whether it is intermolecular or intramolecular. It has been shown[9] that, in the reaction of azoxybenzene (labelled with the ^{15}N isotope) with acetic anhydride (at 230–240 °C) the formation of only 2-hydroxyazobenzene is observed, in which the distribution of the ^{15}N isotope label is not equalised. This shows that the rearrangement proceeds via an intramolecular mechanism.

4-Bromo-*ONN*-azoxybenzene, 4-nitro-*NNO*-azoxybenzene, and 3,3′-dinitro-azoxybenzene have been used as objects of study in two investigations.[8,10] They were subjected to the Wallach rearrangement in sulphuric acid labelled with the ^{18}O isotope under conditions where it is possible to isolate a certain amount of the initial azoxybenzene which failed to react. The isotope composition of the hydroxy-group in the rearrangement product is the same as that of the oxygen in the acid medium. This demonstrates the intermolecular mechanism of the rearrangement.

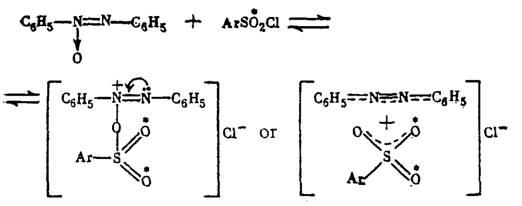
The validity of this conclusion and its independence of the conditions employed, the number of substituents, and their character and positions in the molecule have been confirmed in a study[60] whose authors proposed the mechanism of the Wallach rearrangement illustrated in Scheme 11:

Scheme 11



However, this picture, which is at first sight understandable, becomes much more complex after careful critical analysis. In the first place, the hypothesis that the structure of the monoprotonated form changes in the course of the reaction and even more so the hypothesis that intermediates are formed have not been rigorously proved. Subsequently, the intermolecular mechanism of the Wallach rearrangement was confirmed also for other acid systems. Thus it has been established[22] that, when azoxybenzene is treated with the anhydride of [^{18}O]-labelled benzenesulphonic acid, the oxygen atom of the acid system is found in the hydroxy-group of the final reaction products.

In the reaction of azoxybenzene with [^{18}O]-labelled benzenesulphonyl chloride, which leads to the Wallach rearrangement in the *ortho*-position, the ^{18}O isotope enters the hydroxy-group of the final product.[22] This indicates the intramolecular character of the rearrangement. However, the ^{18}O content in the final product is smaller than its content in benzenesulphonyl chloride, which can be accounted for by the formation of compounds (LVIII) and (LIX). This can also explain the decrease of the ^{18}O content in the *para*-substituted product of the Wallach rearrangement.



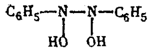
(LVIII) (LIX)

When [^{18}O]-labelled azoxybenzene is used in the Wallach rearrangement, the product is 4-hydroxyazobenzene, in which the ^{18}O content is ~10%.[1] When 4-methyl-*ONN*-azoxybenzene and 2-methyl-*ONN*-azoxybenzene are treated with 80% sulphuric acid, an insignificant amount of ^{18}O is also observed in the product of the Wallach rearrangement.

On the other hand, the study of the rearrangement of 4,4′-dimethylazoxybenzene in concentrated [^{18}O]-labelled sulphuric acid showed that 2-hydroxy-4,4-dimethylazobenzene contains ~70% of ^{18}O.[10] Hence it follows that the product of the Wallach rearrangement of azoxybenzenes is obtained via two mechanisms—intermolecular and intramolecular. Thus the conditions under which the Wallach rearrangement is carried out, the nature of the substituents in the benzene ring, and their positions can influence significantly the ratio of the rates of the process via these two mechanisms. In essence, the problem dealt with here is of central importance for the understanding of the mechanisms of other acid-catalysed rearrangements of nitrogen-containing aromatic compounds. This should be borne in mind in formulating a general mechanism of the Wallach rearrangement.

3. The Generation and Structure of the Intermediate Species When Azoxybenzenes are Treated with Acids

In the first studies of the Wallach rearrangement, it was already suggested that both the initial azoxybenzene and the intermediates formed in the course of the rearrangement may be protonated. On the basis of their own data, according to which the equalisation of the distribution of the ^{15}N label in the final rearrangement product should occur in a symmetrical structure, Shemyakin and co-workers[8] examined the possibility of the formation of compounds (LX)–(LXIII) in the Wallach rearrangement:



$C_6H_5-\underset{HO}{N}-\underset{OH}{N}-C_6H_5$

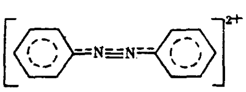
(LX)

$C_6H_5-N\equiv N-C_6H_5$

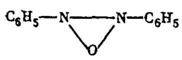
(IV)

$C_6H_5-\overset{+}{N}\equiv\overset{+}{N}-C_6H_5$

(LXI)



(LXII)

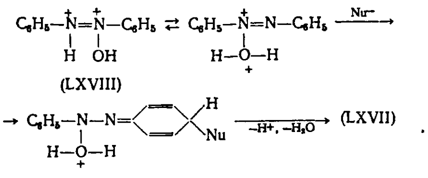


(LXIII)

The *NN*-diol (LX), proposed by Wohl,[61] apparently cannot be formed under the conditions of the Wallach rearrangement, because the hydration necessary for its formation cannot occur in strong acids such as HSO_3F and HSO_3Cl. Shemyakin and co-workers[9] showed that azobenzene (IV) is not an intermediate in the Wallach rearrangement, because the addition of azoxybenzene containing only the ^{14}N isotope to [^{15}N]azoxybenzene under the conditions of the rearrangement did not lead to the dilution of the isotope label in the reaction product—4-hydroxyazobenzene.[9] The structure of the oxide (LXIII) initially explained satisfactorily the experimental data. However, results were later obtained which are difficult to account for from these standpoints. It was found that an increase of the concentration of sulphuric acid from

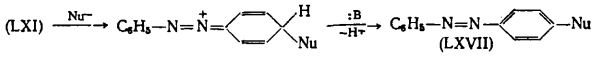
75.3 to 99.99% increases the rate of rearrangement by five orders of magnitude, which indicated an extremely important role of the acidity of the medium. Indeed, kinetic studies of the Wallach rearrangement by Buncel[4] showed that a two proton process takes place. For this reason, the rate-limiting stage of the rearrangement must be the state involving the generation of dicationoid species.

The diprotonated form of azoxybenzene and the dication (LXI) or (LXII), generated by the dehydration of the diprotonated form, are mainly discussed in the literature. The diprotonated form (LXVIII) can be responsible for the Wallach rearrangement, since the reaction of the anion with the medium (or water) results in the formation of the rearrangement product:


(LXVIII)

(LXVII)

On the other hand, the dication (LXI), generated from the diprotonated form of azoxybenzene by dehydration, also affords the products of the rearrangement (LXVII):

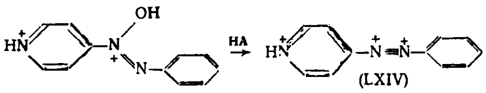

(LXI)

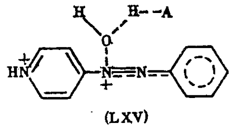
(LXVII)

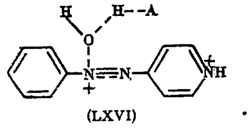
Naturally the question arose which intermediate species are in fact generated in each acid system. The application of ^1H NMR enabled Olah et al.[12] to trace, in relation to azoxybenzene and 4,4′-dichloroazoxybenzene, all the intermediate stages in the Wallach rearrangement—the generation of the mono- and di-protonated forms of azoxybenzene and the formation of a dication of type (LXI). Using ^{19}F and ^{15}N NMR, these intermediate species have been detected analogously[18,63] for decafluoro- and 2,2′,3,3′,5,5′,6,6′-octafluoroazoxybenzenes.

However, one should note that NMR spectroscopy makes it possible to detect only sufficiently long-lived carbonium ions. The data indicated do not therefore necessarily reflect the true picture because the rate-limiting stage may be the generation of a short-lived carbonium ion which is highly reactive. Nevertheless, Olah suggested that a dication of type (LXI) is responsible for the Wallach rearrangement. A number of investigators share this view and the results obtained in the study of the Wallach rearrangement are treated within the framework of Olah's concept. For example, Buncel and Cox[35] invoked the idea of the generation of a cation of type (LXI) to explain the results of the reaction of 2,2′,4,4′,6,6′-hexamethylazoxybenzene with concentrated sulphuric acid (see Scheme 7).

A pathway leading to the rearrangement via the generation of the intermediate trication (LXIV) from the diprotonated form has been put forward.[26] The rate-limiting stage is then the generation process. The authors used this in fact to account for the differences between the rates of rearrangement of the α- and β-isomeric 4-(phenylazoxy)-pyridines. Indeed the formation of the transition state (LXV) from the β-isomer is an energetically favourable process owing to the delocalisation of the charge by the benzene ring, while the transition state derived from the α-isomer (LXIV) is unfavourable from this point of view: [26]


(LXIV)


(LXV)


(LXVI)

The formation of the final product can be readily explained from this standpoint, but the explanation of many other facts encounters difficulties due to the lack of information about the structure of the complexes formed under the real process conditions and about their reactivity. Thus it has been concluded[23] that there is a difference in the pathways leading to the Wallach rearrangement as a function of the acidity of the medium. In relatively weak acids (for example in sulphuric acid at a concentration less than 80%), azoxybenzene is initially protonated at the oxygen atom in the equilibrium stage which is followed by the reversible attack of the nucleophile (probably HSO_4^-) with formation of a substrate of the quinonoid type. Next follows the protonation of this compound at the oxygen atom. In the rate-limiting stage attack by the base takes place (for example by HSO_4^-) with the concerted elimination of water and subsequent rapid hydrolysis, which leads to the final product.

In acids stronger than 80% sulphuric acid, the protonation of the oxygen atom of the azoxy-group is followed by the rate-limiting proton transfer from the undissociated form of the acid (usually acid catalysis) with subsequent elimination of water and the formation of a dication of type (LXV), which is subjected to rapid nucleophilic attack leading to the final product. The claim by Olah et al.[12] that 4-hydroxyazobenzene is formed in the hydrolysis of the dication generated by treating azoxybenzene with $HF—SbF_5—SO$ at −50 °C has been considered as an important argument in support of the formation of a dication of type (LXI). However, the reaction has been studied in detail[18] and it has been found that, under the conditions of the generation of a dication of type (LXI), hydrolysis affords azobenzene in 68–72% yield, while 4-hydroxyazobenzene is formed in small amounts.

We shall quote yet another example of the correction of old experimental data based on a careful analysis of the products of the Wallach rearrangement. It has been reported[57] that treatment of 4-bromoazoxybenzene with with sulphuric acid results in the formation of only 4-bromo-4′-hydroxyazobenzene. However, this study was repeated[29] and it was found that the main product of this reaction is 4-bromoazobenzene, while 4-bromo-4′-hydroxyazobenzene is formed in small amounts.

In contrast to the data of Lukashevich and Kurdyumova,[14] it has been concluded[6] that treatment of azoxybenzene with HSO_3Cl at −10 °C leads to the formation of 26.5% of azobenzene (previously 5% had been found), which appears somewhat strange. We reproduced this reaction and showed that the amount of azobenzene formed is ~5%.[18] Since azobenzene and azobenzene-4-chlorosulphonate have the same R_f, it is difficult to follow by thin-layer chromatography the completeness of the hydrolysis of the sulphate by an aqueous solution of ammonia (as was done by Yamamoto et al.[6]) and the value 26.5% probably refers to a mixture of two substances.

The fact that, as electron-accepting substituents, which reduce the pK_a of azoxybenzenes with a parallel decrease of the capacity of the substrate for diprotonation, are introduced into the benzene ring, the fraction of the azo-compound obtained—the product of the reduction of azoxybenzene—increases, has not so far been explained.

Owing to the probability of the attack by the nucleophile on both benzene rings, in the case of a dication of type (LXI), labelled with ^{14}C in one of the benzene rings, products of the Wallach rearrangement with identical contents of the

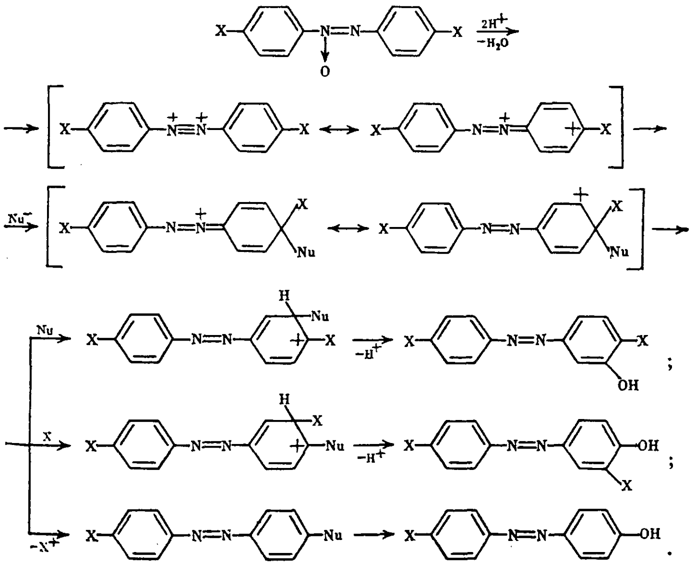
^{14}C label in both rings should be obtained. However, it has been shown for the reaction of [^{14}C]azoxybenzene in sulphuric acid[60] or in the anhydride of benzenesulphonic acid[22] that the ratio of the ^{14}C contents in the benzene rings differs somewhat from 1 : 1. On the other hand, in the diprotonated form of azoxybenzene the shielding of the carbon atoms of both rings, which parallels the magnitude of the positive charge on the atom, is somewhat different (see the ^{13}C NMR data for the diprotonated form of decafluoroazoxybenzene[18]). The small difference in the shielding of the carbon atom can explain the experimental data for the distribution of the ^{14}C label. These factors can indicate that the true intermediate species determining the course of the Wallach rearrangement is the diprotonated form of azoxybenzene.

Owing to the lack of direct experimental evidence, the above conclusions are to a large extent tentative and hence they do not rule out, in principle, other possible explanations.

4. The Interpretation of the "Anomalous" Processes Accompanying the Classical Wallach Rearrangement

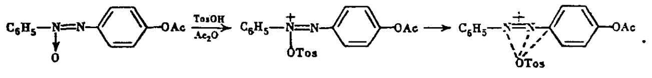
The formation of "anomalous" products on treatment of 4-alkyl- and 4,4′-dialkyl-azoxybenzenes with acids was noted above.[30,33] Assuming the generation of a dication of type (LXI), the appearance of these products can be explained in the following way (Scheme 12):

Scheme 12



The initial diprotonation with subsequent elimination of water leads to the formation of a dication which is attacked by the nucleophile at the carbon atom in the *para*-position. The resulting σ-complex, in which there is a considerable positive charge on C(3), is then converted into the reaction products via several pathways: (a) into 4-hydroxyazobenzene (XXXIII) via the elimination of X^+; (b) into 3-hydroxyazobenzene (XXXI) via a rearrangement with migration of Nu to the 3-position; (c) into 4-hydroxyazobenzene (XXXII) via a rearrangement with migration of X to the 3-position. The ability of X to migrate increases with increase of the electron density at the α-C atom. The group X is readily eliminated if it is able to form a stable carbonium ion [for example, the product (XXXIII) is formed for X = iso–Pr and t–Bu, while the ease of migration of the CH_3 and CH_3CH_2 groups leads to products of type (XXXII)]. The cationoid character of the Wallach rearrangement has been confirmed by these data.

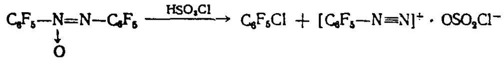
The formation of complex mixtures of products when the Wallach rearrangement is carried out in the toluene-*p*-sulphonic acid–acetic anhydride system can be explained without the concept of the generation of a dication of type (LXI) but via the initial attack of the electrophile from the medium on the oxygen atom of the azoxy-group with subsequent formation of the intermediate (LXVII):[17]



(LXVII)

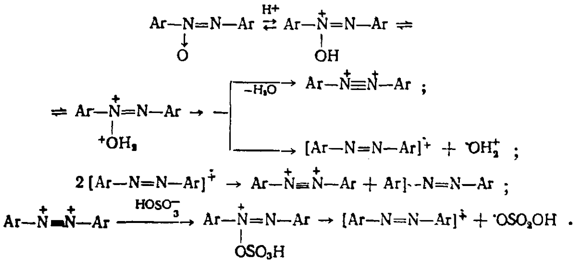
In the cation (LXVII) there is a possibility of attack also in the *unco*-position. In this case a benzenediazonium cation is formed. Its formation has been confirmed by the reaction with toluene, which yields the corresponding biphenyls. It also affords C_6H_5OAc and C_6H_5OTos via the reaction of the intermediate phenyl cation with the anion of the medium.

It has been demonstrated by spectroscopic methods and by the azo-coupling reaction with dimethylaniline[58] that, when decafluoroazoxybenzene is kept in HSO_3Cl for 200 h, the pentafluorobenzenediazonium cation and chloropentafluorobenzene are formed:



$$\underset{\downarrow\atop O}{C_6F_5—N}{=}N—C_6F_5 \xrightarrow{HSO_3Cl} C_6F_5Cl + [C_6F_5—N{\equiv}N]^+ \cdot OSO_2Cl^- .$$

As noted above, the Wallach rearrangement affords in many instances azobenzene, sometimes in predominant amounts. The information about the pathways leading to their formation is fragmentary and frequently contradictory. It has been suggested[19,29] that they are obtained as a result of the disproportionation of the diprotonated form of azoxybenzene, which leads to the azobenzene radical-cation:



$$\underset{\downarrow\atop O}{Ar—N}{=}N—Ar \overset{H^+}{\rightleftarrows} \underset{|\atop OH}{Ar—\overset{+}{N}}{=}N—Ar \rightleftharpoons$$

$$\rightleftharpoons \underset{|\atop {}^+OH_2}{Ar—\overset{+}{N}}{=}N—Ar \to \begin{cases} \xrightarrow{-H_2O} Ar—\overset{+}{N}{\equiv}\overset{+}{N}—Ar ; \\ \longrightarrow [Ar—N{=}N—Ar]^{\dot{+}} + {}^{\cdot}OH_2^+ ; \end{cases}$$

$$2\,[Ar—N{=}N—Ar]^{\dot{+}} \to Ar—\overset{+}{N}{\equiv}\overset{+}{N}—Ar + Ar]\text{-}—N{=}N—Ar ;$$

$$Ar—\overset{+}{N}{\equiv}\overset{+}{N}—Ar \xrightarrow{HOSO_3^-} \underset{|\atop OSO_3H}{Ar—\overset{+}{N}}{=}N—Ar \to [Ar—N{=}N—Ar]^{\dot{+}} + {}^{\cdot}OSO_2OH .$$

By analogy with the reactions of diaryl sulphoxides in sulphuric acid, where the radical-cations of diaryl sulphides were detected by EPR, and the degree of their racemisation was determined using the ^{18}O isotope,[62] Oae and co-workers[19,29] attempted to detect the azobenzene radical-cation but they were unsuccessful. On the other hand, it has been shown for polyfluoroazoxybenzenes[32,63] that azobenzenes are formed only in those cases where dications of type (LXI) are observed, according to ^{19}F and ^{15}N NMR data in the 1 : 1 HF–SbF_5 or 1 : 1 HSO_3F–SbF_5 systems.

If the scheme put forward by Oae and co-workers[19,29] is adopted, then after a time one should observe the diprotonated forms of azobenzenes. However, it has been shown[32] that the signal is 13.6 p.p.m., referring to the diprotonated form of decafluoroazobenzene, is not observed for a solution of decafluoroazoxybenzene in the 1 : 1 HSO_3F–SbF_5 mixture allowed to stand for 20 h at 20 °C, while hydrolysis leads to the formation of decafluoroazobenzene. It has been suggested[32] that the formation of decafluoroazobenzene in this reaction is due to the pronounced oxidising properties of the type (LXI) dication, which oxidises water to hydrogen peroxide, as a result of which the dication itself is reduced to decafluoroazobenzene.

In all cases of the generation of type (LXI) dications from azoxybenzenes, hydrolysis results in the formation of the corresponding azobenzenes. For example, on treatment with the 1 : 1 $(HF-SbF_5)-SO_2$ mixture of 4,4′-difluoroazoxybenzene (−50 °C, 10 min) and 2,2′,4,4′-tetrafluoroazoxybenzene (−10 °C, 30 min), the ^1H NMR spectra revealed the presence of the H_3O^+ cation and the hydrolysis of such solutions results in the formation of 4,4′-difluoro- or 2,2′,4,4′-tetrafluoroazobenzene. The diprotonated form of azoxybenzene is incapable of leading to azobenzenes and the starting materials are recovered in all cases. Thus the dissolution of 4,4′-bis(trifluoromethyl)octafluoroazoxybenzene in the 1 : 1 HSO_3F-SbF_5 or 1 : 1 $HF-SbF_5$ system leads only to the diprotonated form at 20 °C according to ^1H and ^{19}F NMR spectra, while after 50 h signals due to the protons of the H_3O^+ cation appear in the ^1H NMR spectrum. Hydrolysis of this solution leads only to the starting material.

It has been shown[18] that in superacids, where nucleophiles exhibit a low reactivity, the generation of the diprotonated form of azoxybenzene is an insufficient condition for the occurrence of the Wallach rearrangement; the presence of active nucleophilic species is necessary in addition. Thus, in contrast to the reaction in HSO_3Cl, the Wallach rearrangement has not been observed for 2,2′,3,3′,5,5′,6,6′-octafluoroazoxybenzene in the 1 : 1 $(HSO_3F-SbF_3)-SO_2ClF$ (at −40 °C) or 1 : 1 $(HF-SbF_5)-SO_2$ (at −60 °C) systems, where the diprotonated form of azoxybenzene is detected.

We believe that the scheme in which azobenzenes are formed via a dication of type (LXI) on treatment of azoxybenzenes with acids, while the product of the Wallach rearrangement is formed as a result of the reaction of the diprotonated form of azoxybenzene with the nucleophile of the medium, is more likely.

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The survey of data on the Wallach rearrangement permits certain general conclusions. Firstly, its mechanism has not yet been ultimately elucidated. Secondly, similar rearrangements are apparently possible in systems having the N → O group and capable of splitting off water on protonation, generating cationoid species. For example, one may expect that the *N*-oxides of tertiary aromatic amines and *C*N–diarylnitrones undergo a rearrangement in acid media which is of the same type as the Wallach rearrangement.

Thus, in order to understand the entire set of processes occurring in the Wallach rearrangement it is still necessary to solve fairly numerous complex problems. The necessity to proceed to a detailed investigation of the mechanism of the Wallach rearrangement has become self-evident. The solution of this problem can only be achieved by a combined method involving the use of modern physical research techniques. It is possible to differentiate two main groups of problems. One is associated with the study by a spectroscopic method of the electronic structures of the electrophilic species generated in the course of the rearrangement. The other concerns the determination of their true role in the Wallach rearrangement, especially in the rate-limiting stage. There is no doubt that further study of the mechanism of the Wallach rearrangement will significantly expand our ideas about molecular rearrangements.

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The Synthesis of Saturated Cyclic Sulphides

E.N.Karaulova

New syntheses of saturated cyclic sulphides and their functional derivatives are examined. Attention is concentrated on the mode of reaction, the purity of the target products, their yields, and the relation between the structure and properties of cyclic sulphides.

The bibliography includes 142 references.

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I. INTRODUCTION

During the last 10–15 years there has been a sharp growth of the number of studies on the chemistry of organic sulphur compounds. The chemistry of saturated cyclic sulphides has been developing vigorously. They are important models in the study of heteroatomic compounds in petroleum and also serve as the starting materials for the synthesis of polymers, polyfunctional biologically active compounds, and extractants for heavy metals.

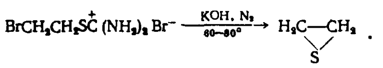
New synthesis of saturated cyclic sulphides during the period 1970–1984 are described in the present review. The yields of the sulphides are indicated (except in those cases where they are not given in the studies quoted or the method of synthesis is not preparative). If reviews or monographs on the relevant topic have been published during the above period, only the most important studies, mainly those published subsequently, are considered.

II. MONOCYCLIC SULPHIDES

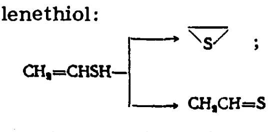
1. Thiirans

The syntheses of thiirans published up to 1976 have been examined in a monograph.[1] The methods of synthesis of thiirans are described systematically in this book in accordance with the types of the ring formation reactions (including the homolytic ring closure via the C=C or C=S bond and heterolytic ring closure as a result of anionotropic or cationotropic transformations). The most important methods of synthesis of thiirans published up to 1980 have been described in a brief review.[2]

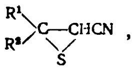
Thiirans have been obtained recently by cyclising S-(2-bromoethyl)isothiuronium bromide on heating with aqueous alkali:[3]



It has been shown[4] that up to 30% of thiiran is formed in the synthesis of ethylenethiol from vinyl chloride and hydrogen sulphide in the vapour phase, probably as a result of the isomerisation of ethylenethiol:

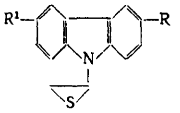


The nitriles of substituted thioglycidic acids



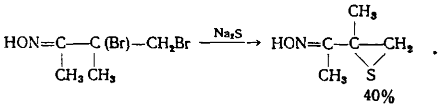
where $R^1 = H$, CH_3, or C_2H_5 and $R^2 = CH_3$ or C_6H_5, have been synthesised[5] by a familiar method involving the condensation of epoxides with potassium thiocyanate; to prevent the desulphurisation of these compounds, it is recommended that the reaction be carried out at pH 6.3–7.

The preparation of carbazolylthiirans with electron-accepting substituents in the carbazole fragment has been described:[6]

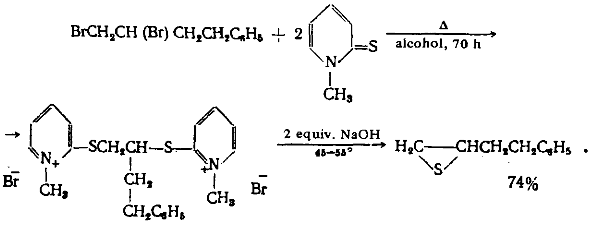


$R=H$, $R^1=Cl$, Br, NO_2; $R=R^1=Br$ or $COCH_3$.

It used to be assumed that the interaction of vicinal dihalogenoalkanes with sodium sulphide leads only to polymers.[1] However, it has been possible recently to achieve the synthesis of thiirans from 1,2-dibromoalkanes. When the oxime of 3,4-dibromo-3-methyl-2-butanone was allowed to react with an excess of sodium sulphide in acetone at 20 °C, 2-(α-hydroxyiminoethyl)-2-methylthiiran was obtained:[7]

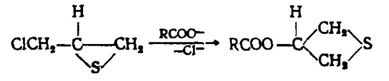


Japanese chemists[8] proposed a method of synthesis of 2-phenylethylthiacycloalkanes from 1-phenylethyl-ω-dibromoalkanes and N-methyl-2(1H)-pyridinethione; thus phenylethylthiiran has been obtained from 1-phenylethyl-1,2-dibromethane:

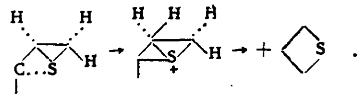


2. Thietans

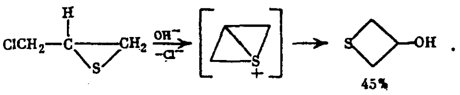
Certain methods of synthesis of thietans (mainly arylthietans) have been examined in the review by Vedejs and Kraft.[2] Nuretdinova and Arbuzov and co-workers investigated the conditions governing the formation of thiiran and thietan derivatives on treatment of ethylthiohalogenohydrins with nucleophiles.[9,10] They found, that, when chloromethylthiiran is treated with sodium and potassium acetates, chloroacetates, methylacrylates, and benzoates in aqueous solutions, 3-acyloxythietans are formed exclusively:



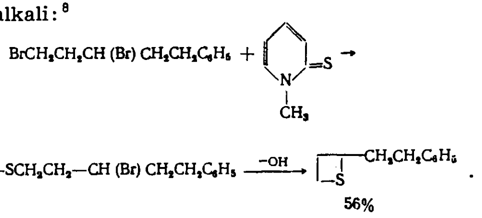
The thiiran–thietan rearrangement then takes place and its mechanism was related by the authors to the formation of an intermediate non-classical thiabicyclobutane cation: the cationotropic transformations of the latter leads, according to Fokin and Kolomiets,[1] to thietan derivatives:



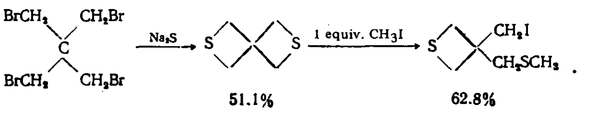
It has been suggested[1] that the conversion of epithiochlorohydrin into 3-hydroxythietan on treatment with aqueous alkali proceeds via the same mechanism:[11]



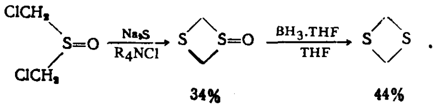
2-Phenylethylthietan can be obtained by prolonged heating of 3,5-dibromo-1-phenylpentane with *N*-methyl-2(1*H*)-pyridinethione and subsequent treatment of the reaction product with aqueous alkali:[8]



A thietan derivative, namely dithiaspiroheptane, has been synthesised by the cyclocondensation of pentaerythrityl bromide with sodium sulphide in aqueous alcohol; on treatment with methyl iodide, the product is converted into 3-iodomethyl-3-methyl-thiomethylthietan:[12]

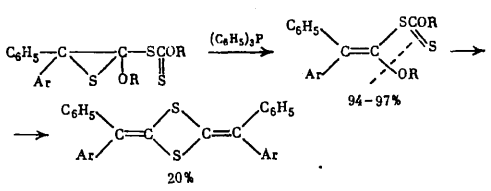


1,3-Diethetan was obtained for the first time in 1982[13] and its properties were investigated. Bis(chloromethyl) sulphoxide cyclises to 1,3-dithietan oxide on treatment with sodium sulphide in an aqueous medium in the presence of a phase transfer catalyst—tricaprilylmethylammonium chloride [the analogous reaction with bis(chloromethyl) sulphide yields only a polymer]. 1,3-Dithietan oxide was reduced to 1,3-dithietan at room temperature by treatment with the borane–tetrahydrofuran complex:

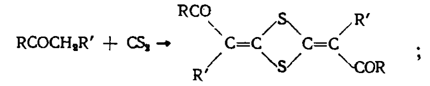


On prolonged storage, 1,3-dithietan is converted into the thioformaldehyde trimer.

1,3-Dithietan derivatives (thioketen dimers) have been obtained[14] by the mild desulphurisation of 2-acylthio-2-alkoxythiirans by tertiary phosphines and subsequent thermolysis of the thioketenals in accordance with the following scheme:

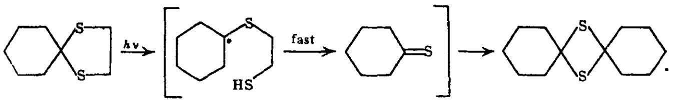


Thioketenal dimers (desaurins) can be obtained in moderate yields by heating carbonyl compounds with carbon disulphide in the presence of potassium hydroxide:[15]

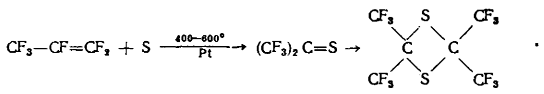


$R=C_6H_5, CH_3;\ R'=H, C_6H_5$.

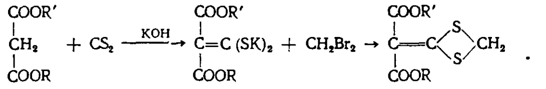
Cyclohexanone thioacetal is converted into spiro-1,3-dithietan on exposure to UV light; the reaction proceeds via a radical mechanism with the intermediate elimination of the radical $\cdot CH_2CH_2SH$ and the formation of cyclohexanethione, which dimerises to spiro-1,3-dithietan:[16]



Hexafluorothioacetone also dimerises to a substituted dithietan:[17]



Dithietanylidenemalonates have been patented as fungicides; it has been recommended that they be obtained by treating malonic acid esters with carbon disulphide in the presence of alkalies; the reaction products are treated with a dihalogenomethane,[18] for example:

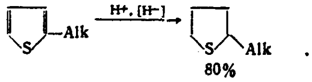


The yields of the required products are 52.8–88%.

3. Thiolans

The syntheses of alkyl- and aryl-thiolans and alkyl- and aryl-thianes, known up to 1969, have been examined in a monograph.[19] Since then new methods of synthesis of the thiolans described previously have been proposed and existing methods have been improved. The purities of the required sulphides have been established by means of gas chromatography and spectroscopic methods. Many thiolans and thianes characterised previously, before the use of these analytical methods, undoubtedly contained considerable admixtures of structural isomers. This must be taken into account in dealing with old data, in particular, with syntheses where dibromoalkanes served as the precursors of thiolans and thianes.

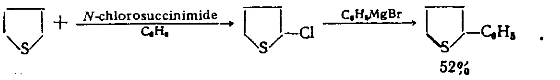
A new method of synthesis of thiolans, including the first member of the series—thiolan itself, involves the ionic hydrogenation of thiophen derivatives.[20] It consists in the successive addition of a proton and hydride ion to the double bonds. Thiophens are acted upon by a trialkylsilane in trifluoroacetic acid:



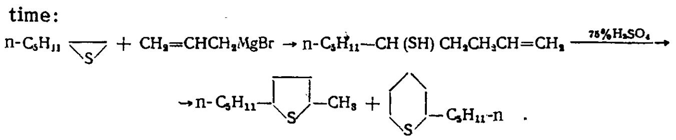
Subsequently the hydrogenating systems were modified[21]—treatment of the corresponding thiophens with the HSi.$(C_2H_5)_3$–HCl/$AlCl_3$ system in methylene chloride produced thiolan, 2-ethylthiolan, 2,5-dimethylthiolan, and, for the first time, 2,5-diphenylthiolan in yields of 25, 80, 75, and 66% respectively. Questions concerning the stereochemistry of disubstituted thiolans were not dealt with by the authors of the above communication.[21]

In order to obtain cyclic sulphides, Crumbie and Ridey[22] hydrolysed alkylthiuronium salts, which is a method widely used previously for the synthesis of alkanethiols. The reaction of 1-chloro-4-iodobutane and one equivalent of thiourea in alcohol yielded 2-(4-chlorobutyl)thiuronium iodide, which was immediately treated with dilute sodium hydroxide. This led to the synthesis of thiolan in 49% yield.

A novel general method of synthesis of 2-substituted cyclic sulphides has been proposed.[23] When unsubstituted cyclic sulphides are chlorinated with *N*-chlorosuccinimide under mild conditions, 2-chlorothiacycloalkanes are formed and are then converted on treatment with methyl- or phenyl-magnesium bromide into 2-substituted thiacycloalkanes (without an admixture of isomers with a different number of members in the ring). 2-Methylthiolan, and for the first time, 2-phenylthiolan were synthesised in this way in satisfactory yields:

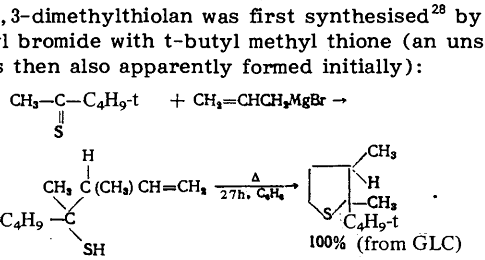


Extremely promising methods of synthesis of thiolans and thianes are based on the cyclisation of unsaturated mercaptans. The use of these reactions makes it possible to develop a general method of synthesis of five- or six-membered cyclic sulphides.[24] The method is based on the interaction of thiirans with allylmagnesium bromide or its homologues, which leads to $\gamma\delta$-unsaturated thiols. Intramolecular cyclisation of the latter via an ionic mechanism leads to sulphides with a five-membered ring and cyclisation via a free-radical mechanism results in the formation of sulphides with six-membered rings; their mixture is usually formed. 2-Methyl-3-n-pentyl- and 2-methyl-3-n-octyl-thiolans,[25] 2-methyl-4-phenylthiolan,[26] and 2-methyl-5-n-pentylthiolan[27] were obtained in accordance with the same scheme for the first time:

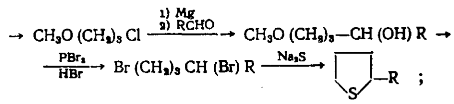


The overall yield of sulphides was 47% and the content of disubstituted thiolans (in the mixture) was 82%.

2-t-Butyl-2,3-dimethylthiolan was first synthesised[28] by treating crotyl bromide with t-butyl methyl thione (an unsaturated thiol is then also apparently formed initially):

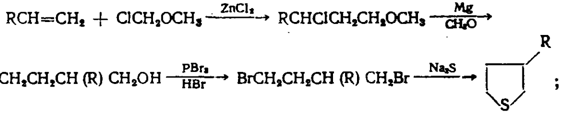


Dibromoalkanes, which are precursors of 2- or 3-substituted thiolans, have been synthesised from chloroalkyl methyl ethers.[29,30] In order to obtain α-substituted 1,4-dibromobutanes, the synthesis was begun with propane-1,3-diol; the substituent was introduced by treating with the corresponding aldehyde the Grignard reagent derived from chloropropyl methyl ether:



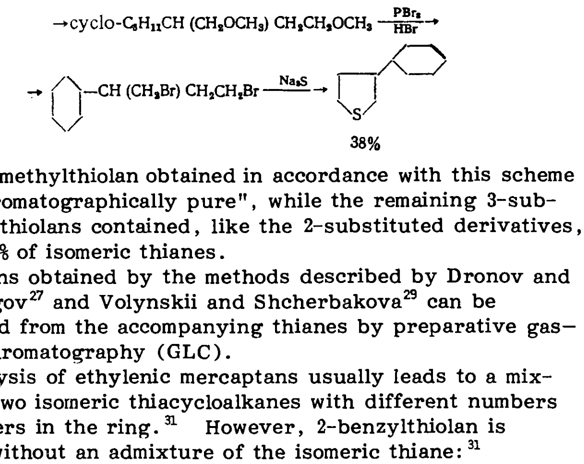
$R = n\text{-}C_3H_7, n\text{-}C_4H_9, n\text{-}C_6H_{13}, C_6H_5.$

The yields of 2-substituted thiolans were 50-80% relative to the dibromides and 27–53% relative to 3-chloropropyl methyl ether. The alkylthiolans obtained in accordance with this scheme contained 17–30% of alkylthianes (with a correspondingly shorter substituent), formed as a result of the cyclisation of the isomeric dibromoalkanes (the bromination method used by the authors leads to a mixture of dibromides which is difficult to resolve). β-Substituted 1,4-dibromobutanes were synthesised from α-olefins:



$R{=}CH_3, C_4H_9, C_5H_{11}, C_6H_{13}$.

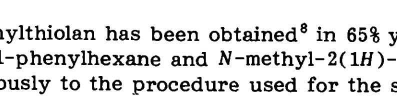
3-n-Butyl- and 3-n-hexyl-thiolans were obtained for the first time. The yields of 3-substituted thiolans (relative to the dibromides) were 64–81%. Volynskii and Shcherbakova[29,30] synthesised for the first time also 3-cyclohexylthiolan using the more readily available styrene rather than vinylcyclohexane:



The 3-methylthiolan obtained in accordance with this scheme was "chromatographically pure", while the remaining 3-substituted thiolans contained, like the 2-substituted derivatives, about 20% of isomeric thianes.

Thiolans obtained by the methods described by Dronov and Krivonogov[27] and Volynskii and Shcherbakova[29] can be separated from the accompanying thianes by preparative gas-liquid chromatography (GLC).

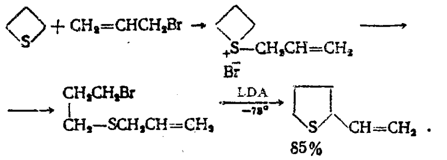
Photolysis of ethylenic mercaptans usually leads to a mixture of two isomeric thiacycloalkanes with different numbers of members in the ring.[31] However, 2-benzylthiolan is formed without an admixture of the isomeric thiane:[31]



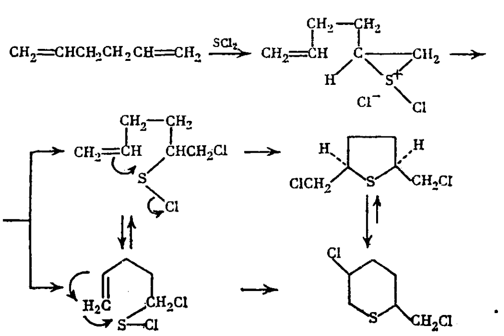
2-Phenylethylthiolan has been obtained[8] in 65% yield from 3,6-dibromo-1-phenylhexane and *N*-methyl-2(1*H*)-pyridinethione analogously to the procedure used for the synthesis of 2-phenylethylthietan described above.

New functional derivatives of thiolan have been obtained both from the corresponding acyclic precursors and by introducing functional groups into thiolans.

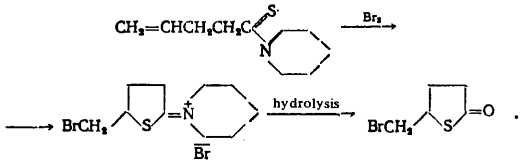
2-Vinylthiolan has been obtained from thietan and allyl bromide.[32] The allylthietanium bromide formed on interaction of these reactants is unstable and rearranges to allyl 3-bromopropyl sulphide, which is converted into 2-vinylthiolan on treatment with lithium diisopropylamide (LDA):



It has been shown recently[33] that, contrary to Lautenschlager's data,[34] the reactions of sulphhr dichloride with hexadiene are not regiospecific. This results in the formation of *cis*-2,5-dichloromethylthiolan and 5-chloro-2-chloromethylthiane (60:40). At 20 °C isomerisation takes place gradually and at thermodynamic equilibrium the ratio is 35:65 and the overall yield of adducts is 80%. However, they could be separated only after the preliminary oxidation to sulphones (the latter were separated by fractional crystallisation):

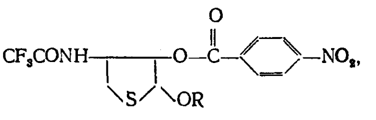


5-Substituted 2-thiolanones are obtained[35] by brominating or iodinating the thioamides of allylacetic acid, which entails heterocyclisation and the formation of halogenomethylpentamethyleneimmoniathiolan halides in yields up to 81%, for example:



The initial thioamides are obtained by refluxing the amides $CH_2 = CHCH_2CH_2CONR_2$ [NR_2 = piperidinyl, morpholinyl, $NHCH_2C_6H_5$, $N(CH_3)_2$, or $NHCH_3$] with P_2S_5 in benzene; it has been established that the "iodocyclisation" reaction is of first order with respect to iodine and thioamides.

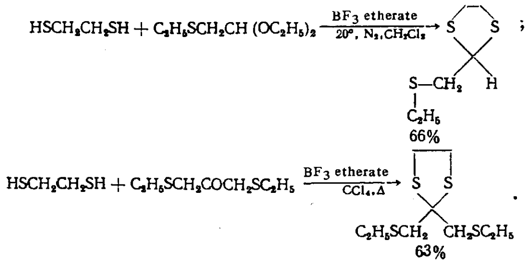
The starting materials for the synthesis of adriamycin analogues, namely the trisubstituted thiolans



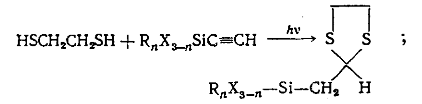
where R = $COCH_3$, $CH(CH_3)_2$, or cyclohexyl, have been obtained[36] from 3,4-dihydroxythiolan by means of successive reduction, trifluoroacylation, esterification, and alkoxylation.

Certain formation reactions of dithiolans and trithiocarbonates, derived from 1,3-dithiolan-2-thiones, have been described in a monograph.[1]

Numerous 2-substituted 1,3-dithiolans have been synthesised in recent years. The heterocycle is usually constructed from ethane-1,2-dithiol. The condensation of this dithiol with the diethylacetal of 2-(ethylthio)acetaldehyde or with 3,7-dithia-5-nonanone yielded 2-(ethylthiomethyl)- and 2,2-di(ethylthiomethyl)-1,3-dithiolan:[37]

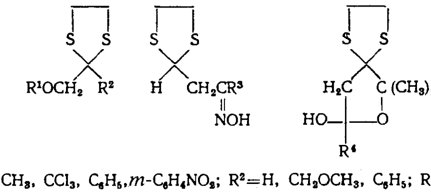


2-Silyl-1,3-dithiolans are formed on photochemical interaction of ethane-1,2-dithiol with ethynylsilanes:[38]



n=1—3, R=Alk, X=Cl, AlkO, AcO .

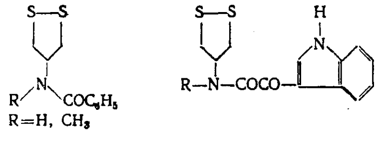
2-Substituted 1,3-dithiolans have been synthesised in order to obtain compounds with fungicidal properties:[39]



R^1=CH_3, CCl_3, C_6H_5, *m*-$C_6H_4NO_2$; R^2=H, CH_2OCH_3, C_6H_5; R^3=C_6H_5, 2-thienyl; R^4 = 2-furyl, 2-thienyl.

Among these compounds, spiro-1,3-dithiolans, especially the compound with R^4 = 2-thienyl, proved to be extremely active against phytophthora on tomatoes.

4-*N*-Acyl-1,2-dithiolans have also been synthesised by the direct acylation of 4-amino-1,2-dithiolans in order to obtain biologically active preparations:[40]



4. Thianes

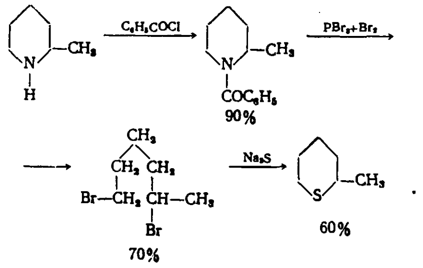
During the last 15 years many new mono- and poly-alkyl and mono- and poly-aryl-thianes have been synthesised.

The first member of the series (thiane) has been obtained by two new procedures: in 80% yield from 1-chloro-5-iodopentane and thiourea, analogously to the procedure described above[22] for thiolan, and in 76% yield from ethylene sulphide and allyl-magnesium bromide[41] (in accordance with the procedure proposed a year earlier[24]). Kondo and Negishi[41] directed the cyclisation of the initially formed thiol towards the formation of thianes by the following procedure: magnesium thiolate was decomposed with a solution of ammonium chloride and the resulting unpurified thiol was immediately refluxed in the presence of a radical reaction initiator—azobisisobutyronitrile.

3-Methyl-, 4-methyl- and (for the first time) 4-phenylthianes have been obtained in 70—74% yields by an analogous procedure involving the reaction of ethylene sulphide with methylallyl-, crotyl-, or cinnamyl-magnesium bromide.[41] 2-Methyl- and 2,2-dimethyl-thianes have been obtained in 60% yields from allylmagnesium bromide and propylene or isobutylene sulphide.[41] The absence of an admixture of the isomeric thiolans indicated the selective cleavage of the less sterically hindered C–S bond in the ethylene sulphides.[41]

The mixture containing 75% of 2-n-pentylthiane has been synthesised in 68.7% yield from allylmagnesium bromide and heptene sulphide;[27] the thiane was isolated by GLC (the intermediate decene-5-thiol was cyclised by exposure to UV radiation). 4-n-Pentylthiane (yield 47%) and 4-n-octylthiane (yield 44%) have been obtained analogously from ethylene sulphide and the corresponding alkenylmagnesium bromide, while 3-phenylthiane has been obtained from styrylethylene sulphide and allylmagnesium bromide in ~25% yield.[26]

2-Methyl, 4-methyl-, and 4-t-butyl-thianes have been synthesised from the corresponding alkylpiperidines in accordance with the scheme[42]

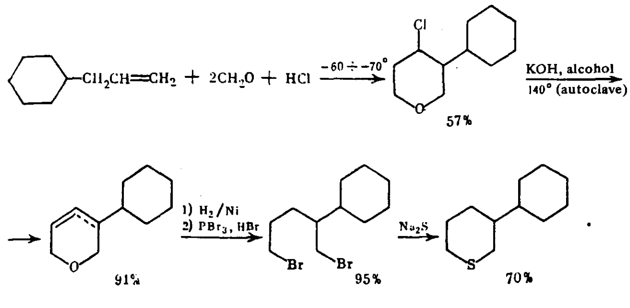


The synthesis includes only three stages (provided of course that alkylpiperidines are available).

2-Methylthiane and (for the first time) 2-phenylthiane have been obtained[23] from thiane in a manner analogous to the above synthesis of 2-phenylthiolan[23] (the yields were respectively 51 and 56%).

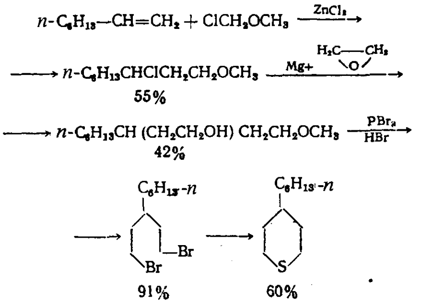
2-Phenylthiane has been synthesised[8] from 3,7-dibromo-1-phenylheptane and N-methyl-2(1H)-pyridinethione in 40% yield.

1,5-Dibromopentanes, which are precursors of 3- and 4-substituted thianes, have been obtained from α-olefins.[43,44] In order to obtain β-substituted 1,5-dibromopentanes, 3-alkyltetrahydropyrans were initially synthesised by condensing α-olefins with paraformaldehyde:[43]



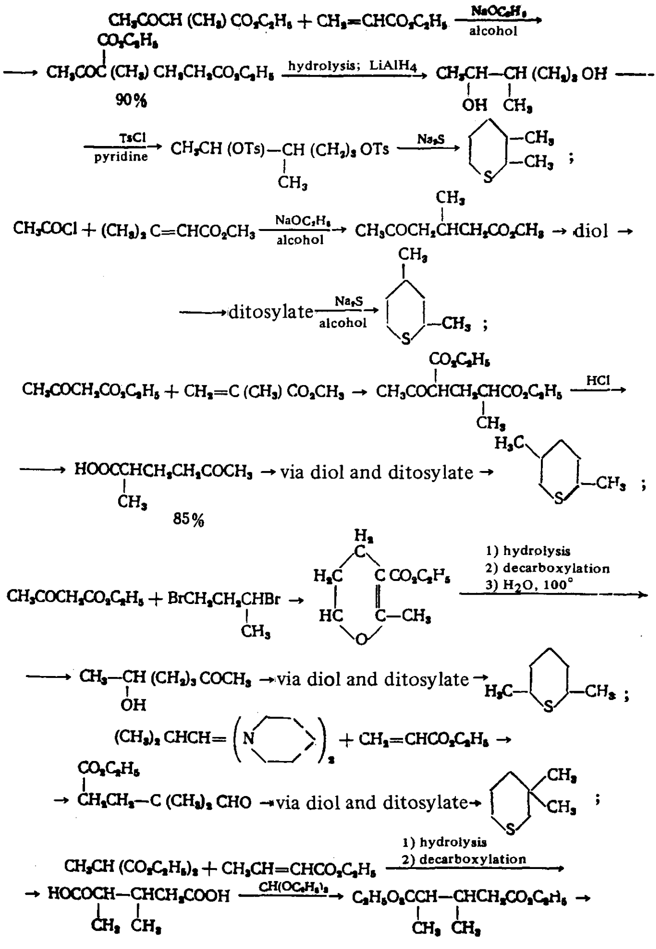
The authors modified the method of the opening of the tetrahydropyran ring having substituted sulphuric acid by phosphorus tribromide. The increase in the cost of the synthesis is compensated by the fact that the yield and purity of the dibromides are then significantly improved. This procedure has been used successfully by the authors in subsequent studies for the cleavage of ethers. 3-n-Butyl-, 3-n-hexyl- and (for the first time) 3-cyclohexyl-thianes were synthesised in accordance with the above scheme[43] in 85, 88, and 70% yields respectively.

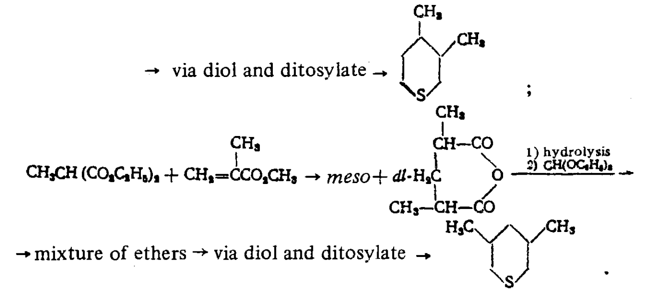
In the synthesis of γ-substituted 1,5-dibromopentanes, carbon chain extension was achieved by two procedures:[44]



Using this method, the authors[44] obtained 4-methyl-, 4n-butyl-, 4n-pentyl-, and 4-phenyl-thianes and also (for the first time) 4n-hexyl- and 4-cyclohexyl-thianes, the yields being respectively 86, 68, 80, 40, 60, and 70%.

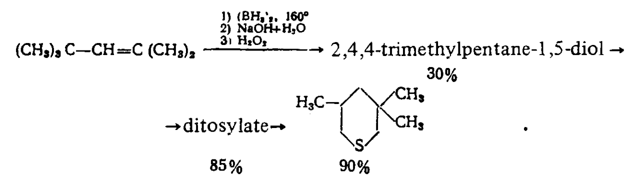
In order to investigate the conformations by ^{13}C NMR, extensive syntheses of dimethylthianes were carried out[42] in 1977; 13 thianes were synthesised for the first time, namely the *cis*- and *trans*-isomers of 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dimethylthianes and 3,3-dimethylthiane. All these compounds are obtained by reducing the corresponding precursors with lithium tetrahydroaluminate to 1,5-diols (90% yields), which were then converted into 1,5-di(toluene-p-sulphonate) (yields up to 80%) and their condensation with Na_2S afforded mixtures of the *cis*- and *trans*-substituted dimethylthianes (yields 65–85%). The stereoisomers were separated by preparative GLC. All the precursors of 1,5-diols were obtained from fully available compounds in accordance with the schemes



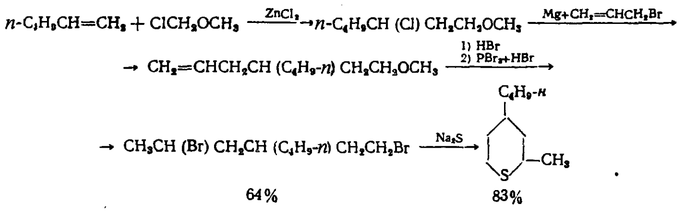


cis-3,5-Dimethylthiane can also be obtained without using preparative GLC: *meso*- and *dl*-dimethylglutaric anhydride are separated by crystallisation, the *meso*-form (yield 25%) is reduced with lithium tetrahydroaluminate to *meso*-2,4-dimethylpentane-1,5-diol and the latter is converted with PBr_3 into the dibromo-derivative (yield 80%), which is treated with Na_2S; the yield of 3,5-dimethylthiane is 75%.

The same workers[42] obtained for the first time 3,3,5-trimethylthiane in accordance with the scheme



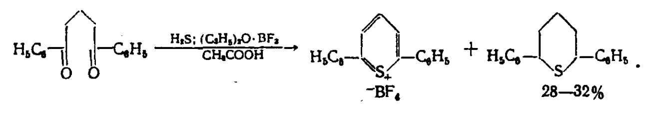
The authors[45] used the scheme proposed previously[44] for the synthesis of 4-substituted thianes in order to obtain 2,4-disubstituted thianes. The growth of the carbon chain, achieved with the aid of allyl bromide, made it possible to introduce a methyl group in the 2-position:



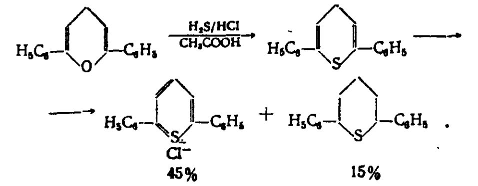
Using this scheme, the authors[45] synthesised for the first time 4-n-butyl-2-methyl-, 2-methyl-4-n-pentyl-, and 2-methyl-4-phenyl-thianes in the form of mixtures of *cis*- and *trans*-isomers (yields 83–87%): the stereoisomers of 2,4-dialkylthianes were separated by GLC. On the other hand, a mixture of the *cis*- and *trans*-2-methyl-4-phenylthianes was oxidised and the resulting mixture of stereoisomeric 1-oxides was separated by fractional crystallisation, after which the 1-oxides were reduced with lithium tetrahydroaluminate to *cis*- and *trans*-2-methyl-4-phenylthianes.[46] Having replaced hydrobromic acid by DBr, the same authors[46] obtained 2-monodeuterio-4-n-butylthiane in 74% yield by means of the same scheme.

2,2-Diphenylthiane was obtained for the first time by hydrogenating *gem*-diphenylthiacyclohexene over 10% Pd/C in a mixture of equal amounts of alcohol and ethyl acetate.[47] Hydrogenation of polyaryl(alkyl)-4*H*-thiopyrans over the same catalyst (in alcohol at 100 °C and a 5% atm hydrogen pressure) led to the corresponding polyaryl(alkyl)thiane—2,6-diphenyl-, 4-methyl-2,6-diphenyl, 2,4,6-triphenyl-, 3,5-dimethyl-2,6-diphenyl-, and 3-methyl-2,4,6-triphenylthianes—in 72–80% yields.[48]

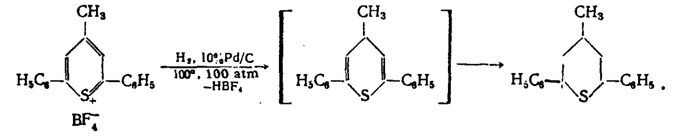
Several further preparative methods of synthesis of 2,6-disubstituted thianes have been proposed,[49,52] for example, from the corresponding 1,5-disubstituted pentane-1,5-diones:[49,50]



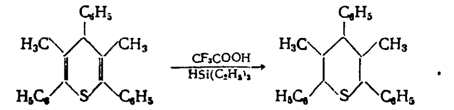
As shown by Kharchenko and Chalaya,[51] 2,6-diphenylthiane is formed as a result of the disproportionation of 2,6-diphenyl-4*H*-thiopyran:



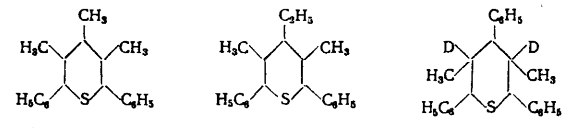
2,6-Diphenylthianes and thiapyrylium salts can be readily separated using their different solubilities in non-polar solvents. Diphenylthianes are also formed smoothly on hydrogenation of thiapyrylium salts[52] (yield 65–79%) with the initial formation of 4*H*-thiopyrans, for example:



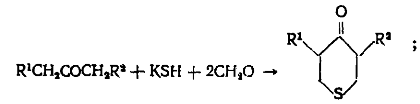
The ionic hydrogenation reaction can be used to obtain thianes from 4*H*-thiopyrans. The corresponding thianes have been obtained from polysubstituted 2,6-diphenyl-4*H*-thiopyrans by treatment with trifluoroacetic acid and an active hydride ion donor—triethylsilane:[53]



The use of CF_3COOD in ionic hydrogenation established that the double bond in 4*H*-thiopyrans is protonated in the C(3)- and C(5)-positions;[53] polysubstituted thianes were obtained for the first time in the above study:[53]



Few functional derivatives of thianes have been synthesised in recent years. A single-stage method of synthesis of disubstituted tetrahydro-1-thiopyran-4-ones has been proposed recently.[54] They were obtained by the thioalkylation reaction—the condensation of ketones containing at the carbonyl group two methylene groups having equal reactivities, with potassium hydrogen sulphide and formaldehyde in alcohol (with brief heating at 50 °C); the yields are 23–72.5%:

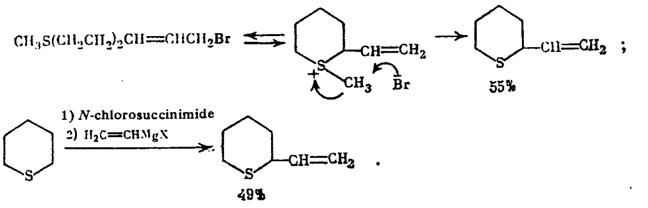


$R^1=R^2=C_2H_5,\ C_3H_7,\ n\text{-}C_4H_9,\ C_7H_{15};\ R^1=C_6H_5,\ R^2=CH_3.$

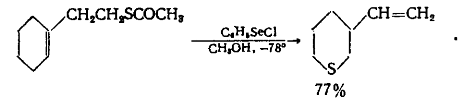
Ketosulphides are mixtures of stereoisomers with the *cis*-isomer predominating slightly; it is recommended that they be used as extractants for palladium ions.

When 6-dimethylamino-5-methylhex-2-en-4-one methiodide is treated with a solution of sodium sulphide at room temperature, 2,5-dimethyl-4-thianone is formed (yield 67%). 2,3-Dimethyl-4-thianone has been obtained analogously (yield 76%).[55]

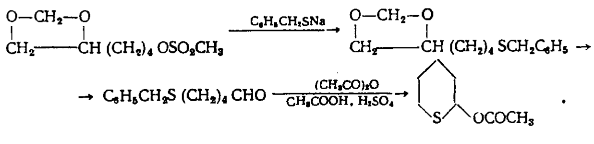
α-Vinylthiane has been obtained[56] by cyclising 7-bromohept-5-enyl methyl sulphide and also from thiane:



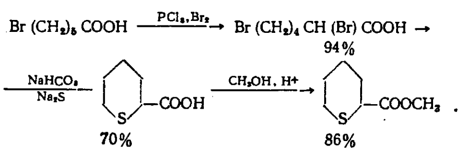
β-Vinylthiane is formed as a result of the cyclisation of acetylthioethylcyclohex-1-ene by treatment with benzeneselenyl chloride at a low temperature:[57]



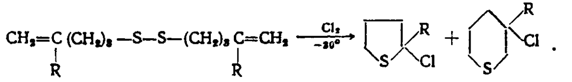
When butyl-lithium and then tetrahydrothiopyran-4-one are added to cyclopentadiene, fulvene—4-cyclopentadienylidenethiane—is formed as an unstable yellow liquid (yield 75%).[58] 2-Acetoxythiane has been synthesised by a fairly complex procedure:[59] the benzyl derivative was obtained from the methanesulphonate of the formal of hexane-1,2,6-triol and sodium benzylmercaptide and, after hydrolysis and oxidative cleavage, was converted into benzyl 4-formylbutyl sulphide; the latter was subjected to acetolysis in a mixture of acetic anhydride and acetic acid containing sulphuric acid:



There exists yet another method of synthesis of 2-acetoxythiane,[60] but the number of stages is likewise fairly large:

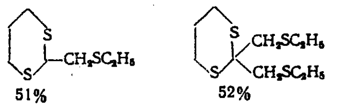


The chlorination of dipent-4-enyl disulphides yields a mixture of α-chlorothiolans and β-chlorothianes; when equilibrium is attained, the thianes predominate.[61] The reaction apparently proceeds via a stage involving the formation of unsaturated sulphenyl chloride:

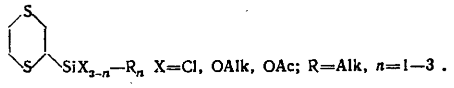


For R = H, the thiolan : thiane ratio is 80 : 20 (under the conditions of kinetic control) or 18 : 82 (under equilibrium conditions); for R = CH_3, the corresponding ratios are 95 : 5 and 4 : 96.

2-(Ethylthiomethyl)- and 2,2-di(ethylthiomethyl)-1,3-dithianes have been synthesised by the reaction of propane-1,3-dithiol with the diethylacetal of 2-ethylthioacetaldehyde or with 3,7-dithia-5-nonanone, analogously to the method described above for 1,3-dithiolans:[37]



The photochemical interaction of ethynylsilanes with ethane-1,2-dithiol results in the formation of 2-silyl-1,4-dithianes together with 1,3-dithiolans (see above):[38]



At −196 °C carbon monosulphide combines with hydrogen chloride to form the chloride of thioformic acid, which is rapidly converted into 2,4,6-trichloro-1,3,5-trithiane in ~50% yield on raising the temperature; 2,4,6-tribromo-1,3,5-trithiane has been obtained analogously by reaction with hydrogen bromide in ~75% yield.[62]

Some data on the relations between the structure and properties of the substituted thiolans and thianes. The dependence of the boiling points and retention volumes of alkylthiolans and alkylthianes (including the individual stereoisomers) on the number of substituents and their positions in the ring has been investigated.[63,64] Calculations showed that 2,4-dialkylthianes do not obey the Auwers–Skita rule—the *trans*-isomers have lower boiling points than the *cis*-isomers. Subsequently the applicability of the "reverse" Auwers–Skita rule to 2,4-disubstituted thianes (and to their 1,1-dioxides) was demonstrated experimentally in a number of investigations.[42,45,46]

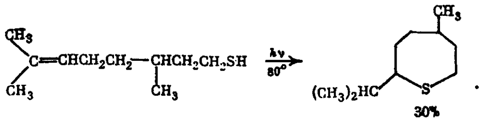
The characteristics of the chemical shift in the ^{13}C NMR spectra of methylthiolans have been examined;[65] the ^{13}C NMR spectra of thiane, twelve of its mono-di, and tri-methyl derivatives, 4-t-butylthiane, and two tetradeuteriothianes have been discussed by Willer and Eliel[42] and those of 1,3-dithianes by Eliel et al.[66] The ratios of the conformers in dimethylthianes and the conformational free energies of the methyl group in the 2-, 3-, and 4-positions in the thiane ring have been determined from the data obtained.

Krapivin and Perepelitchenko[67] investigated the ^{13}C NMR spectra of thianes with long alkyl (C_4–C_5) and aryl substituents and concluded that the steric disposition of substituents in 2,4-disubstituted thianes can be established from the chemical shifts of the ^{13}C nuclei in the 6-position in the thiane ring.

5. Sulphides Containing More Than Six Members in the Ring

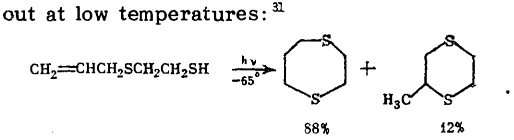
Thiepans have been synthesised by methods analogous to those examined above for thiolans and thianes. Thiepan has been obtained in 34% yield from 1-chloro-6-iodohexane and thiourea.[22] By treating thiepan with *N*-chlorosuccinimide in benzene, Tullen and Bennet[23] obtained α-chlorothiepan and treatment of the latter with methyl- or phenyl-magnesium bromide afforded 2-methylthiepan (yield 66%) and (for the first time) 2-phenylthiepan (yield 56%).

The photochemical cyclisation of 2,6-dimethyloct-2-ene-8-thiol results in the formation of 2-isopropyl-4-methylthiepan without an admixture of the stereoisomeric thiane:[31]



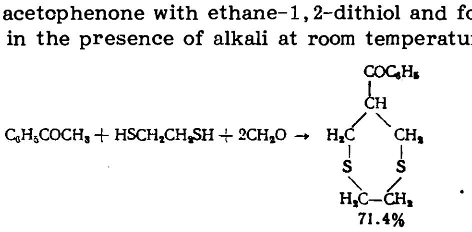
2-Phenylethylthiepan has been synthesised[8] from 3,8-dibromo-1-phenyloctane and N-methyl-2(1H)-pyridinethione in 56% yield.

A mixture of isomeric dithiacycloalkanes (overall yield 45%), with the 1,4-dithiepan predominating, is formed when the photochemical cyclisation of allyl 2-mercaptoethyl sulphide is carried out at low temperatures:[31]



2-(Ethylthiomethyl)- and 2,2-di(ethylthiomethyl)-1,3-dithiepans have been obtained from butane-1,4-dithiol by reaction of the latter with the diethylacetal of 2-ethylthioacetaldehyde or 3,7-dithia-5-nonanone respectively.[37]

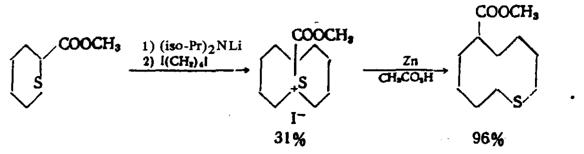
6-Benzoyl-1,4-dithiepan has been synthesised by thioalkylating acetophenone with ethane-1,2-dithiol and formaldehyde in the presence of alkali at room temperature:[68]



Numerous macrocyclic sulphur compounds, namely saturated macrocyclic sulphides, have been synthesised in recent years using noble metals as complex-forming agents and extractants. The methods of synthesis of a wide variety of macrocyclic sulphides, including saturated compounds, published up to 1974, have been examined in the review of Bradshaw and Hui.[69] The results of latter studies (1974–1983) have been very successfully surveyed in two other reviews.[70,71]

A modification of one of the methods of synthesis of macrocyclic sulphides, consisting in the interaction of ω-dihalides with ω-dimercaptans in an alkaline medium at high dilution,[69] merits consideration; instead of the usually employed alkali metal mercaptides, Setzer et al.[72] used a benzyltrimethylammonium salt, which led to a significant increase of the yield of the required products. Under the conditions of high dilution (in absolute methanol), benzyltrimethylammonium, di(2-mercaptoethyl) sulphide, and, simultaneously, 1,2-dibromoethane were made to react whilst heated. 1,4,7-Trithiacyclononane was obtained in 4.4% yield instead of the 0.04% yield obtained previously. Other analogous syntheses have been carried out (the yields expressed as percentages are indicated in brackets): 1,4-dithiepan (65) from ethane-1,2-dithiol and 1,3-dibromopropane; 1,5-dithiacyclooctane (46) from propane-1,3-dithiol and 1,3-dibromopropane; 1,4-dithiacyclooctane (14) from butane-1,4-dithiol and 1,2-dibromoethane; 1,5-dithiacyclononane (9) from the same dithiol and 1,3-dibromopropane; 1,6-dithiacyclodecane (1.5) from the same dithiol and 1,4-dibromobutane. 2-Phenylethylcyclononane has been obtained in 50% yield from 3,10-dibromo-1-phenyldecane and N-methyl-2(1H)-pyridine thione.[8]

6-Methoxycarbonylthiacyclodecane can be obtained fairly easily from 2-methoxycarbonylthiane via a bicyclic sulphonium salt:[60]



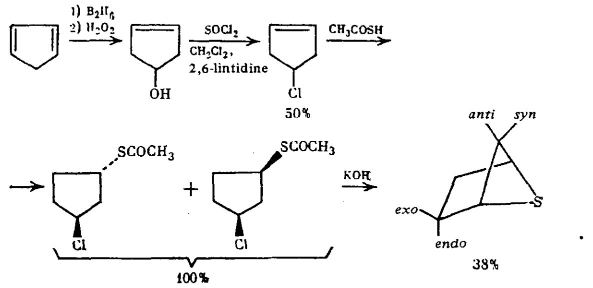
In discussions of the properties of macrocyclic sulphides, it has been noted[69,73] **that the melting points of thiacrown ethers increase with increase of the number of sulphur atoms** in each analogous series: the larger (compared with oxygen) sulphur atom renders the rings less mobile and the number of conformations in the liquid state and hence the entropy of fusion therefore decrease. Furthermore, the more symmetrical compounds have higher melting points. For the same number of sulphur atoms in the ring, the melting point regularly diminishes as the number of CH_2 groups separating the sulphur atoms rises and very large rings (containing more than 12 members) resemble two parallel chains linked at each end by methylene bridges or a sulphur atom.

III. POLYCYCLIC SULPHIDES

1. Thiabicycloalkanes

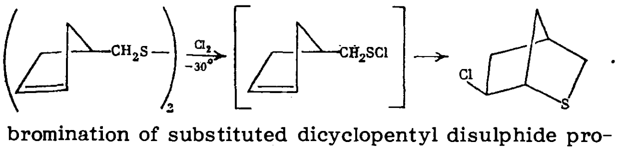
After the methods of synthesis of polycyclic sulphides had been surveyed in a monograph,[19] more than forty new thiabicycloalkanes have been obtained. These are mainly methyl- or phenyl-thiabicyclooctanes and also thiabicyclononanes—both unsubstituted and with methyl or aromatic substituents and thiabicyclodecanes with the same substituents. Most of the methods of synthesis of these compounds have been developed by Soviet workers.

Tabushi et al.[74] obtained the first representative of thiabicyclohexanes—5-thiabicyclo[2.1.1]hexane—from cyclopentadiene in accordance with the scheme

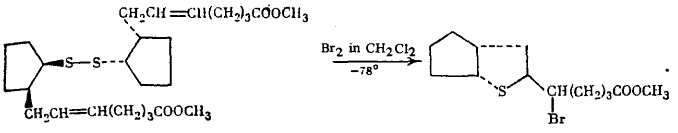


The addition of thioloacetic acid to chlorocyclopentene proceeds quantitatively and leads to a mixture of stereoisomeric 3-acetylthio-1-chlorocyclopentanes. The mixture is added to a boiling aqueous alcoholic solution of potassium hydroxide, whereupon the required product is formed from the *trans*-isomer (it is purified by preparative GLC).

6-*exo*-Chloro-2-thiabicyclo[2.2.1]heptane, its methyl analogue, and 7-*exo*-chloro-2-thiabicyclo[3.2.1]octane are obtained in quantitative yields by the intermolecular cyclisation of sulphenyl chlorides—the intermediates formed on chlorination of unsaturated disulphides at a low temperature:[75]

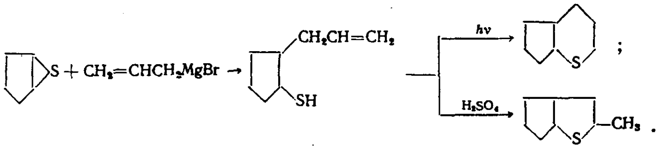


The bromination of substituted dicyclopentyl disulphide proceeds similarly—3-(1-bromo-4-methoxycarbonylbutyl)-2-thiabicyclo[3.3.0]octane has been obtained:[76]

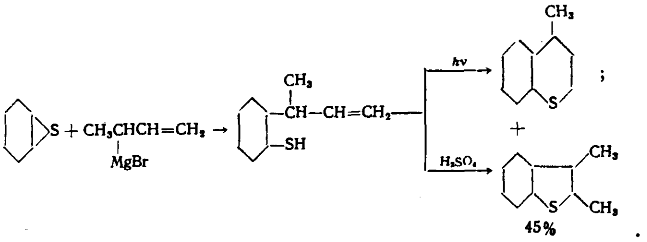


Thiabicyclooctanes, thiabicyclononanes, and thiabicyclodecanes have been synthesised successfully by condensing cycloalkene sulphides with allylmagnesium bromide and its derivatives. The reaction proceeds analogously to that examined above for thiolans and thianes.[24]

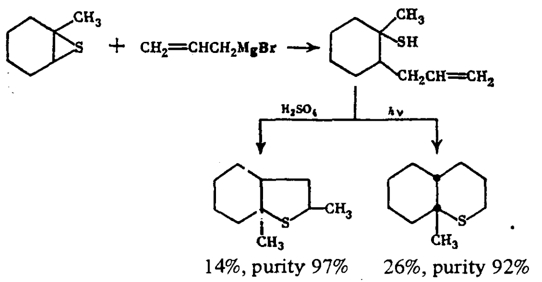
2-Allylcyclopentanethiol has been obtained from cyclopentene sulphide and allyl-magnesium bromide.[77] Its cyclisation on UV irradiation affords 2-thiabicyclo-[4.3.0]-nonane with an admixture of 3-methyl-2-thiabicyclo[3.3.0]-octane (ratio 97: 3, overall yield 42%). In cyclisation on treatment with sulphuric acid, the ratio of these structural isomers is reversed, but the overall yield of thiabicycloalkanes is low (13%). The authors explained this by the difficulty of the formation of two *trans*-joined five-membered rings:[78]



It has been shown[79] that 2-(α-methyl-β-propenyl)cyclohexanethiol is formed from cyclohexene sulphide and crotylmagnesium bromide, which reacts in the form of 3-magnesiobromobut-1-ene; its cyclisation on irradiation gives rise to a mixture of 8,9-dimethyl-7-thiabicyclo[4.3.0]nonane (2,3-dimethyl-1-thiahydrindan) and 5-methyl-2-thiabicyclo[4.4.0]-decane (4-methyl-1-thiadecalin) in an overall yield of 50%; cyclisation on treatment with sulphuric acid results in the selective formation of a thiahydrindan derivative. In both procedures the cyclisation is non-stereospecific. The pure structural isomers are obtained with the aid of GLC.



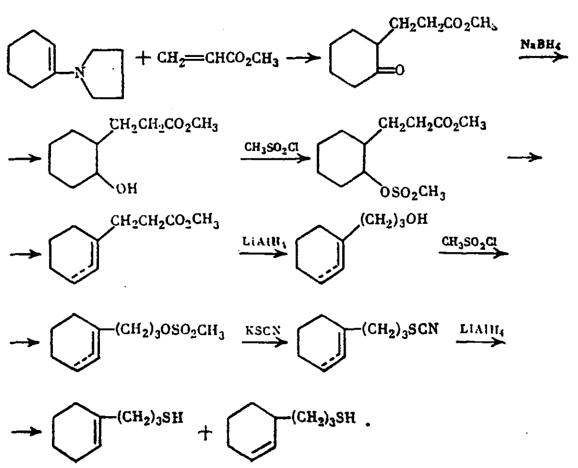
When 1-methylcyclohexene sulphide reacts with alkylmagnesium bromide, the C–S bond at the carbon atom attached to the larger number of hydrogen atoms is broken; the cyclisation of the thiol leads to thiabicycloalkanes with the methyl substituent at the ring junction in the *trans*-position relative to the angular hydrogen atom—6,8-dimethyl-7-thiabicyclo[4.3.0]nonane (2,8-dimethyl-1-thiahydrindan) and 1-methyl-2-thiabicyclo[4.4.0]decane (9-methyl-1-thiadecalin).[80] Although the yields are low for both cyclisation procedures, the processes are fairly selective. The subsequent purification via mercury complexes makes it possible to obtain "chromatographically pure" thiabicycloalkanes:



Fairly pure 8-methyl-7-thiabicyclo[4.2.0]nonane (2-methyl-1-thiahydrindan)[81] and 2-thiabicyclo[4.4.0]decane (1-thiadecalin)[41,81] have also been obtained in 52 and 67% yields from cyclohexene sulphide and allylmagnesium bromide; they were previously synthesised by another method.[19,82]

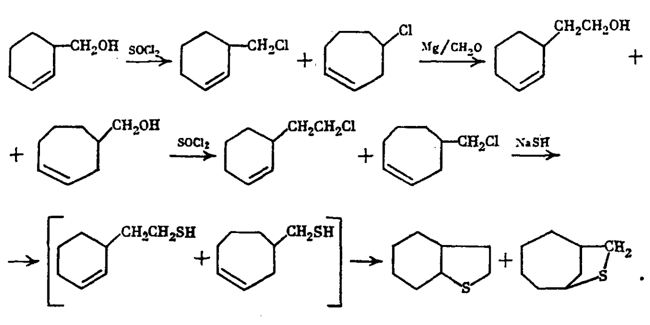
Claus and Vierhapper[83] used azobisisobutyronitrile for the radical cyclisation of *trans*-allyl cyclohexanethiols (cf. Kondo and Negishi[41]). 2-Thiabicyclo[4.4.0]decanes are then formed preferentially. With the aid of this initiator, 4-, 7-, and 10-methyl-*trans*-2-thiabicyclo[4.4.0]decanes were obtained for the first time. The same authors synthesised 4-, 6-, 8-, and 10-methyl-*cis*-2-thiabicyclo[4.4.0]decanes[83] using the fact that the radical cyclisation of 3-mercaptopropylcyclohexenes under the influence of the same initiator proceeds preferentially with formation of *cis*-joined thiabicyclodecanes.

The syntheses of such mercaptans are extremely laborious—for example a mixture of 1- and 3-(3-mercaptopropyl)cyclohexenes, cyclisation leads to *cis*-2-thiabicyclo[4.4.0]decanes, is obtained from pyrrolidinocyclohexene in 8 stages:



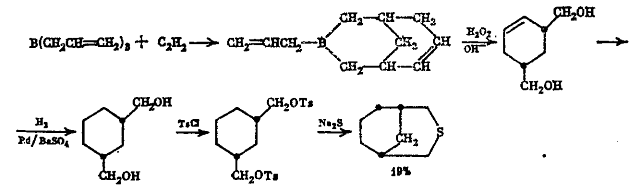
The content of *cis*-2-thiabicyclo[4.4.0]decane in the mixture after the cyclisation of there mercaptans is 68%. It is isolated by separating the complexes with mercury(II) chloride or by preparative GLC; methyl-*cis*-2-thiabicyclo[4.4.0]-decane has been obtained[83] using analogous schemes. The configurations and conformations of the compounds synthesised were identified[84] by means of ^{1}H and ^{13}C NMR spectroscopy.

Four unsubstituted bridged thiabicyclononanes have been synthesised. *cis*-7-Thiabicyclo[4.2.1]nonane mixed with *cis*-7-thiabicyclo[4.3.0]nonane (*cis*-1-thiahydrindan) was obtained[85] from 3-hydroxymethylcyclohexene according to the scheme

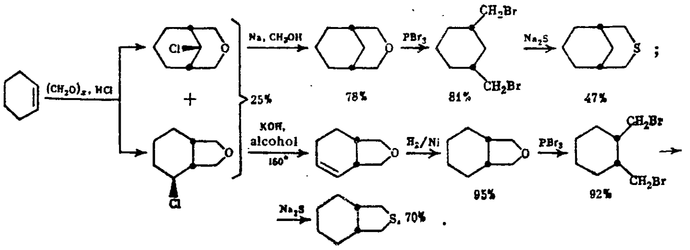


The formation of a mixture of such sulphides is a result of ring expansion on chlorination of hydroxymethylcyclohexene and also the cyclisation of thiols only at the nearest (relative to the substituent) end of the double bond. The overall yield of the mixture of sulphides in the last stage of the scheme is 90% and they are formed in approximately equal amounts; the mixture is separated by preparative GLC.

7-Thiabicyclo[3.3.1]nonane has been synthesised; its precursor—1,3-di(hydroxymethyl)cyclohexane—was obtained from acetylene and triallylborane:[86]



The same sulphide has been recently synthesised[87] by a simpler procedure:

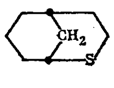


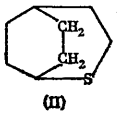
The second, isomeric chloromethylation product "was not wasted"—the authors used it to synthesise 8-thiabicyclo-[4.3.0]nonane, which had been previously obtained by Birch et al.[88] by a procedure involving a greater number of stages.

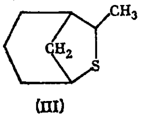
A two-stage method has been proposed for the synthesis of bridged thiabicyclooctanes and thiabicyclononanes from vinylcyclohexenes.[89,90] When vinylcyclohexenes interact with sulphur dichloride, intramolecular cyclisation adducts, namely isomeric dichlorothiabicycloalkanes, are formed (together with oligomeric products). The adducts are subjected to reductive dechlorination whereupon mixtures of thiabicycloalkanes are formed and are then resolved by preparative GLC.

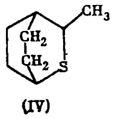
In the course of the exchange of chlorine atoms for hydrogen, skeletal isomerisation takes place, the extent of which depends on the presence of methyl groups in the vinylcyclohexenes, their positions, the nature of the reducing agent, and the reduction conditions.

Unsubstituted thiabicycloalkanes have been obtained[89] from 4-vinylcyclohexene and sulphur dichloride on reduction by diisobutylaluminium (the yield of their mixture was 23%): 2-thiabicyclo[3.3.1]nonane (I) and 2-thiabicyclo[3.2.2]-nonane (II), and also methyl-substituted derivatives: *exo*- and *endo*-7-methyl-6-thiabicyclo[3.2.1]octanes (III) and 3-methyl-2-thiabicyclo[2.2.2]octane (IV):

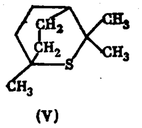

(I)

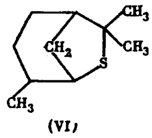

(II)

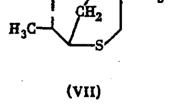

(III)

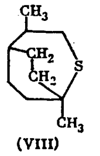

(IV)

A mixture of thiabicycloalkanes (its yield was 86% after reductive dechlorination) has been synthesised analogously from 4-isopropenyl-1-methylcyclohexene.[90] 1,3,3-Dimethyl-2-thiabicyclo[2.2.0]octane (V), 4,7,7-trimethyl-6-thiacyclo-[3.2.1]—octane (VI), 4,8-dimethyl-2-thiabicyclo[3.3.1]-nonane (VII), and its epimer were isolated; the reduction of the adduct with sodium tetrahydroborate results in the formation also of considerable amounts of 1,4-dimethyl-2-thiabicyclo[3.2.2]nonane (VIII):

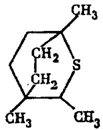

(V)

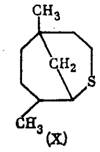

(VI)


(VII)

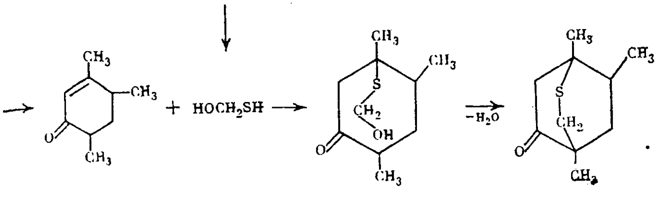

(VIII)

After the reduction of the adducts of sulphur dichloride and 1,4-dimethyl-4-vinyl-1-cyclohexene with diisobutylaluminium, a mixture of 1,3,4-trimethyl-2-thiabicyclo[2.2.2]-octane (IX) and 5,8-dimethyl-2-thiabicyclo[3.3.1]nonane (X) was obtained in proportions of 3 : 1 in 19% yield:


(IX)

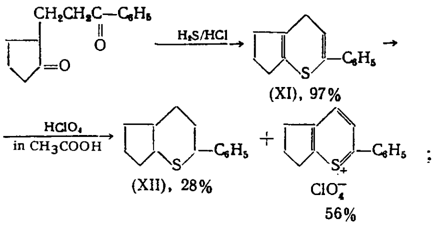

(X)

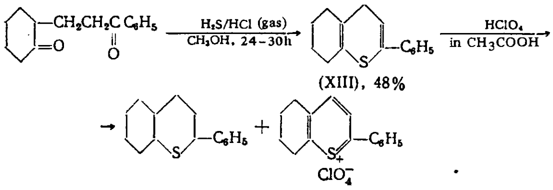
The thioalkylation of ethyl methyl ketone[91] makes it possible to obtain extremely simply (in one stage) 1,4,5-trimethyl-7-thiabicyclo[2.2.2]octan-2-one in 20% yield (the remainder consists of polymeric products):



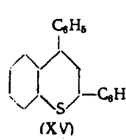
During the 1970's, the interaction of "semicyclic" 1,5-diketones with hydrogen sulphide in the presence of protic acids was investigated. The initial 1,5-diketones are obtained by the Michael reaction from cyclopentanone and arylideneacetophenones.[92] The reaction of diketones with hydrogen sulphide proceeds at room temperature. Aryl-substituted polymethylene-4*H*-thiapyrans are formed and in the presence of strong acids disproportionate to a mixture of polymethylenethiopyrylium salts and arylthiabicycloalkanes.[93] The latter are formed in low yields (of the order of 30%). However, the ease of their isolation from the mixture (readily separated from thiopyrylium salts by extraction with ethylhexane) makes up for this disadvantage.

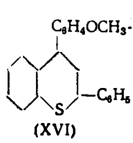
Aryl-2-thiabicyclo[4.3.0]nonanes are obtained from cyclopentanone derivatives and aryl-2-thiabicyclo[4.4.0]decanes are synthesised from cyclohexanol derivatives, for example:[94]

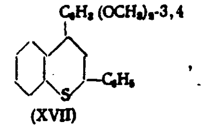




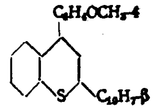
The compounds


(XV)

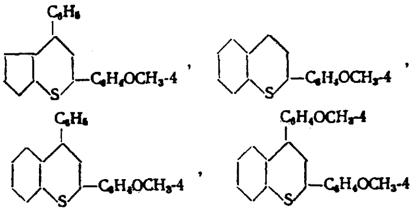

(XVI)



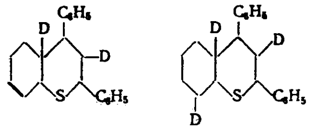
(XVIII)



have been obtained in the same way.[92,94] Compounds (XII) and (XIV)–(XVII) as well as other thiabicycloalkanes have been synthesised[95] in accordance with an analogous scheme from the corresponding 1,5-diketones and hydrogen sulphide, but in this case the reaction was in trifluoroacetic acid:

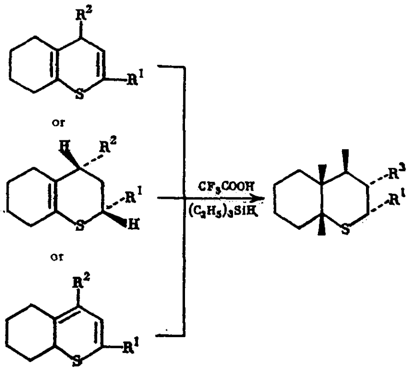


The study of the reaction of polymethylene-4H-thiopyrans with deuteriotrifluoroacetic acid[96] made it possible to establish the site of protonation in the disproportionation reaction; di- and tri-deuterio-3,5-diphenyl-2-thiabicyclo[4.4.0]decanes were then obtained for the first time:



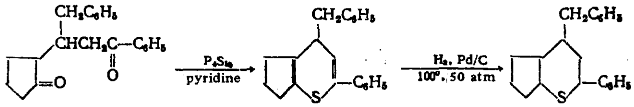
13%

Aryl-2-thiabicycloalkanes have been obtained in high yields by the catalytic hydrogenation (over Pd/C) of the corresponding 4H-thiopyrans, such as, for example, compounds (XI) and (XIII).[97] Compounds (XIV)–(XVII) have also been obtained by the ionic hydrogenation of condensed dihydro-4H- and dihydro-6H-thiopyrans (the yields were respectively 61, 60, 59, and 27%).[98] Regardless of the position of the double bond in the initial heterocycle and the degree of unsaturation, the *cis, cis, cis*-isomers are then formed:



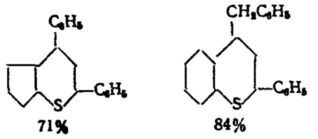
Compound (XV), obtained in 25% yield by the disproportionation of the corresponding thiopyran derivative, also has the *cis,cis,cis*-configuration.[99]

The initial condensed 4H-thiopyrans have also been synthesised from 1,5-diketones and P_4S_{10} by Kupranets's procedure,[92] for example:



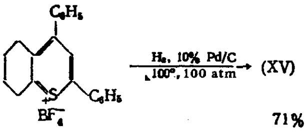
66%

Compounds (XII) and (XIV)–(XVII) as well as thiabicycloalkanes have been obtained analogously:[97,100]



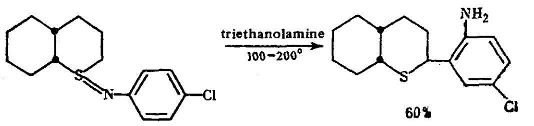
71% 84%

Hydrogenation of salts derived from arylthiochromylium also leads to thiabicycloalkanes:[52]



71%

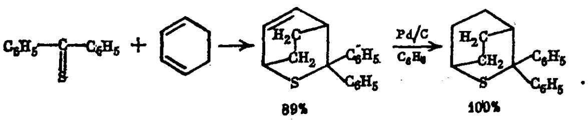
3-(2-Amino-5-chlorophenyl)-2-thiabicyclo[4.4.0]decanes can be obtained by the rearrangement of sulphimides—2-(p-chlorophenylimino)-2-thiabicyclo[4.4.0]decanes.[101] The synthesis and stereochemistry of the formation of the latter has been examined in detail in a review:[93]



60%

The product of the rearrangement is isolated by chromatography. The yields of the products of the rearrangement of sulphimides derived from methyl-2-thiabicyclo[4.4.0]decanes are 16–71% (depending on the conformation of the initial compound). If there is no steric hindrance, the rearrangement proceeds with a high degree of stereospecificity (>95%): shlphimides with an equatorial or axial S–N bond afford products with an equatorial or axial aryl substituent respectively.

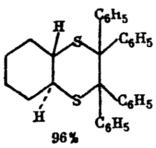
The initial compound for the synthesis of αα-disubstituted (relative to the sulphur atom) thiabicycloalkanes may be thiobenzophenone: its condensation with cyclohexa-1,3-diene led to the formation of 3,3-diphenyl-2-thiabicyclo[2.2.0]oct-5-ene which was then hydrogenated:[47]



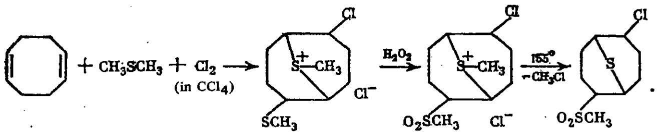
89% 100%

trans-2-Thiabicyclo[4.4.0]decan-5-one has been obtained in 50% yield from 1-(3-dimethylaminopropanoyl)cyclohexene and hydrogen sulphide in the presence of sodium acetate; the analogous reaction with 1-(3-dimethylaminobutanoyl)cyclohexene leads to the 3-methyl derivative in 78% yield.[102] These compounds can also be obtained from the methiodides of the above bases and sodium sulphide.[55,93]

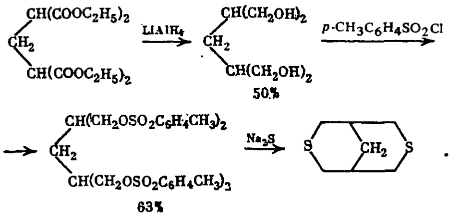
A review[103] devoted to the photocycloaddition of carbonyl compounds of olefins quotes the reaction of thiobenzophenone with cyclohexene which resulted in the formation of 3,3,4,4-tetraphenyl-2,5-dithiabicyclo[4.4.0]decane with a *trans*-junction between the rings:



The synthesis of pesticides based on 2-chloro-6-methanesulphonyl-9-thiabicyclo[3.3.1]nonane has been patented;[104] the nonane derivative was synthesised from cycloocta-1,5-diene and dimethyl sulphide in accordance with the scheme



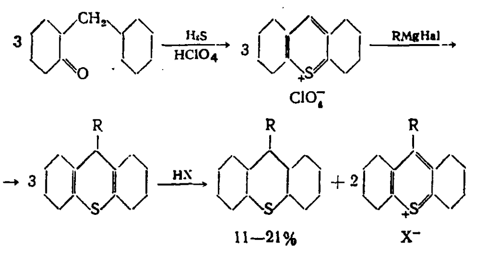
3,7-Dithiabicyclo[3.3.1]nonane has been synthesised[105] using the scheme



2. Thiatricycloalkanes

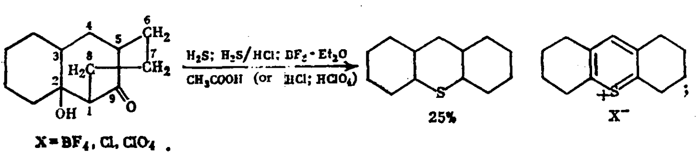
The synthesis of thiapolycycloalkanes with the aim of modelling the sulphur compounds in petroleum has acquired special importance in connection with the more extensive investigation of the composition and properties of the high-molecular-weight component of petroleum. However, in contrast to the syntheses of the thiamonocyclo- and thiabicycloalkanes, the methods of synthesis of thiapolycycloalkanes have developed little in recent years. This is apparently associated with the difficulty of constructing their bicyclic or tricyclic precursors.

The synthesis of perhydrothioxanthene from cyclohexylidenecyclohexanone has been examined in a monograph;[19] 9-substituted perhydrothioxanthenes have been obtained using the same scheme:[106,107]



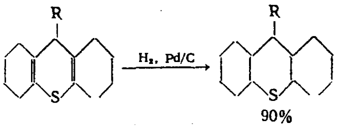
$R = C_2H_5, C_3H_7, C_6H_5$, $X = ClO_4, FeCl_4, Cl, CF_3COO, Br$,

Perhydrothioxanthene has also been obtained from 2-hydroxy-2,3-tetramethylenebicyclo[3.3.1]nonan-9-one:[108]



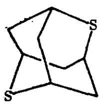
$X = BF_4, Cl, ClO_4$.

Perhydrothioxanthenes can be obtained in satisfactory yields by the catalytic hydrogenation of thioxanthylium salts[52] and also octahydrothioxanthenes:[97]

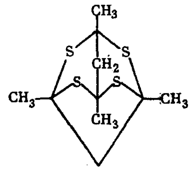


$R = H, CH_3$.

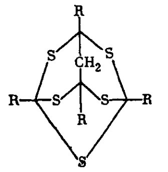
The syntheses of 2,6-dithiaadamantane (XVIII) from thiabicyclo[3.3.1]nona-2,6-diene, of tetrathiaadamantane (XIX) from dithioacetylacetone, and of tetrathiaadamantane, pentathiaadamantane (XX), and hexathiaadamantanes from β-dicarbonyl compounds and thioacetic acid have been considered in a review:[109]



(XVIII)

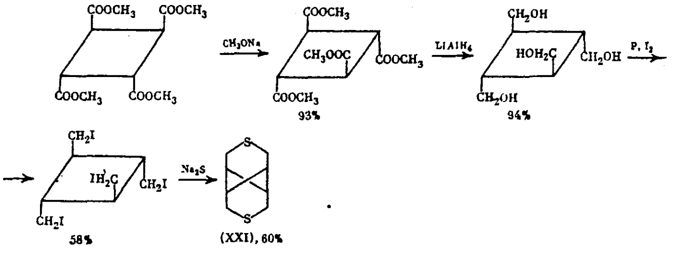


(XIX)



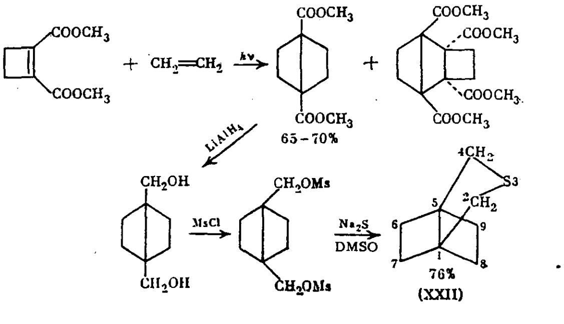
(XX)

4,9-Dithiatricyclo[4.4.0.$0^{2,7}$]decane (XXI) has been synthesised by a comparatively simple procedure.[110] The photodimerisation of dimethyl fumarate in the solid phase yielded tetramethoxycarbonylcyclobutane and from the latter *trans, trans, trans*,-1,2,3,4-tetra(iodomethyl)cyclobutane was obtained. Sodium sulphide is added into its solution in absolute ethanol with the aid of the Soxhlet apparatus and the sulphide (XXI) is obtained:

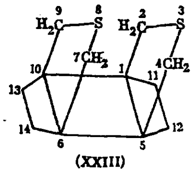


A characteristic feature of the structure of the sulphide (XXI) is the flattening of the six-membered ring. It is of interest that there is a maximum at 246 nm in its UV spectrum. The authors[110] explain this by the result of the interaction of the σ-orbitals of the four-membered ring and the *p* electrons of the sulphur atom.

3-Thiatricyclo[3.2.2.$0^{1,5}$]nonane or 3-thia[3.2.2]propellane (XXII) has been synthesised[111] by the photochemical cycloaddition of ethylene to 1,2-dimethoxycarbonylcyclobutene:

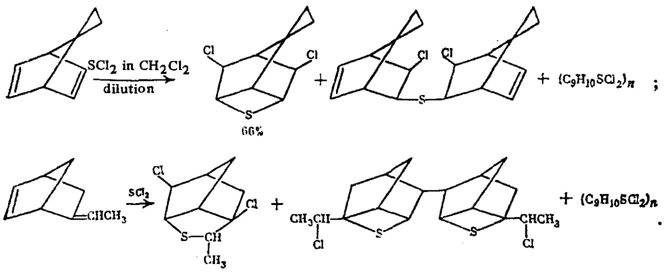


The pentacyclic sulphide (XXIII) was obtained[111] from the photodimer, formed in the first stage of the synthesis, via the same sequence of reactions; its yield in the last stage of the synthesis was 64%:



(XXIII)

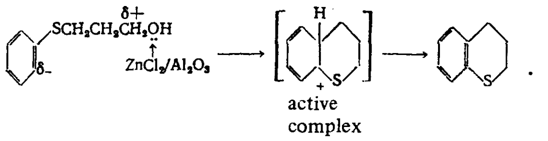
Adducts, consisting of chloro-derivatives of saturated tricyclic sulphides with a thiaskeletal structure have been obtained from bicyclic dienes and sulphur dichloride:[112]



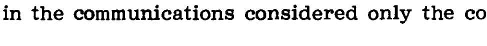
3. Semiaromatic Sulphides

The advances in the synthesis of "semiaromatic" polycyclic sulphides (i.e. those where at least one CH_2 group adjoins the sulphur atom in the ring) have been associated in recent years with the study of the [3,3]sigmatropic ("thio-Claisen") rearrangement of alkenyl aryl sulphides and principally with the development of the syntheses of thiacyclophanes.

The reactions of alkenyl aryl sulphide and also certain thiophenols were carried out in the presence of acid catalysts.[113–116] This resulted in the formation of thiaindans and thiachromans. Thus, when 1-phenylthio-3-propanol is passed at 300 °C over alumina on which zinc chloride has been deposited, thiachroman is formed (31–35%):[113, 115]

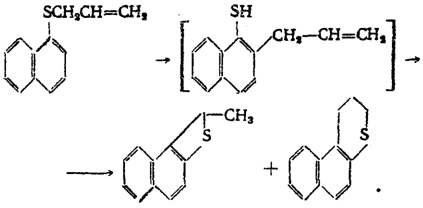


2-Methyl-1-thiaindan is formed in an insignificant yield from allyl phenyl sulphide over this catalyst, while over alumina, which is a less acid catalyst, the yield is better (33%).[114] Under these conditions, thiaindans are partly dehydrogenated to thiaindenes (in the presence of zeolite, the overall yield of 2-methyl-2-thiaindan and 2-methylthiaindene is 47%.[115]) The reaction of but-3-enyl phenyl sulphide in the presence of 20% $ZnCl_2/Al_2O_3$ at 30 °C takes place with formation of 33% of 4-methylthiochroman.[116] The formation of 15% of a tricyclic "semiaromatic" sulphide, namely cyclopentano-2,3-dihydrobenzothiophen, from cyclopentenyl phenyl sulphide has been noted:[116]

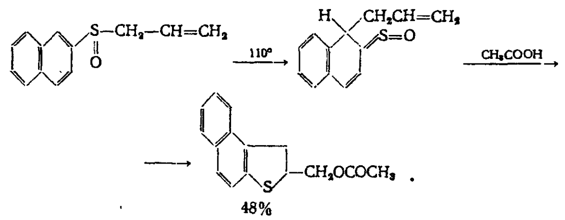


The catalytic synthesis of such semiaromatic sulphides from alkenyl phenyl sulphides is attractive by virtue of its simplicity but in the communications considered only the contents of the sulphide in the catalytic reaction mixture, determined by GLC analysis, are given, while the yields of the individual derivatives of thiaindans and thiachromans are not indicated.

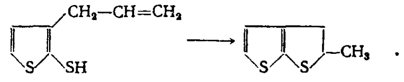
The "thio-Claisen" rearrangement has continued to be extended to new objects under traditional conditions—with heating in the absence of a solvent or in aprotic solvents. Heating of allyl 1-naphthyl sulphide at 190 °C in quinoline leads to the formation of a mixture of approximately equal amounts (59:41) of tricyclic derivatives of thiaindan and thiachroman:[117]



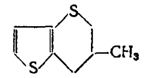
Japanese investigators[118] heated allyl 2-naphthyl sulphoxide in the presence of acetic acid and dimethylformamide and obtained a functional derivative of a tricyclic semiaromatic sulphide:



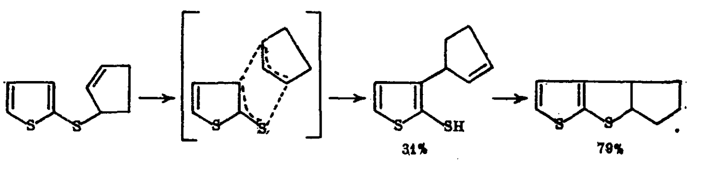
Semiaromatic sulphides have also been synthesised from thiophen derivatives.[119–121] In this case too mixtures of dihydrothiolen and dihydrothiopyran are usually formed. The synthesis where only one of the possible structural isomers is formed are of preparative interest. Thus, when 3-allylthiophen-2-thiol is heated in hexamethylphosphoramide, only 2-methyl-2,3-dihydrothieno[2,3b]thiophen is formed in 50% yield:[119]



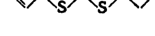
The thermal rearrangement of β-methylallyl 3-thienyl sulphide leads to only 3-methylthieno[3,2*b*]dihydrothiopyran:[119]



3-(Cyclopent-2-enyl)-thiophen-2-thiol cyclises at 120 °C in quinoline with formation of cyclopentano-2,3-dihydrothieno-[2,3*b*]thiophen; the initial thiol is obtained beforehand from cyclopent-2-enyl 2-thienyl sulphide:[120]

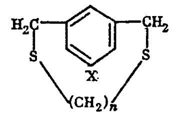


The corresponding thiol is obtained analogously in a low yield (12–14%) from cyclopent-2-enyl 2-benzothienyl sulphide and its cyclisation affords cyclopentano-2,3-dihydrobenzothieno[2,3*b*]thiophen:[121]



The synthesis of cyclophanes—cyclic compounds containing one or several benzene rings joined by polymethylene bridges in the *o*-, *m*-, or *p*-positions—has developed in recent years. These compounds serve as convenient objects for the study of a large number of problems in theoretical organic chemistry. Thiacyclophanes usually serve as precursors of cyclophanes, being converted into the latter, for example, with the aid of the Stevens rearrangement. The methods of synthesis of thiacyclophanes have been considered in detail in two reviews.[69,70]

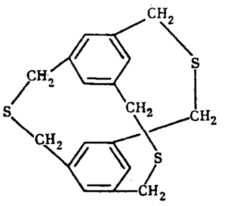
A general method of synthesis of thiacyclophanes involves the reaction of the corresponding dibromo-derivatives with dithiols. For example, more than 100 dithia-*meta*-cyclophanes have been synthesised and investigated in two studies,[69,122] for example, compounds of the type



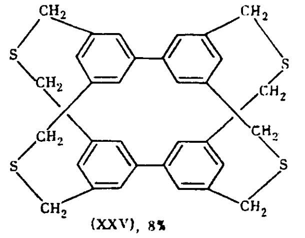
$n = 2-10$, X=H,F,Cl,Br,CH_3,CH_3O,CN

They were obtained by the reaction of equimolar amounts of αω-bismercaptans with the corresponding αα′-dibromo-*m*-xylenes in a basic medium (yields 3–90%). High dilution is used in the synthesis of thiacyclophanes of medium size.[123]

The precursors of two- and three-layer cyclophanes (also referred to as "cage compounds") are bridged polythiacyclophanes, for example, compounds (XXIV) and (XXV):

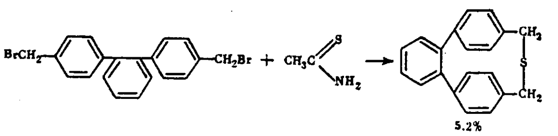


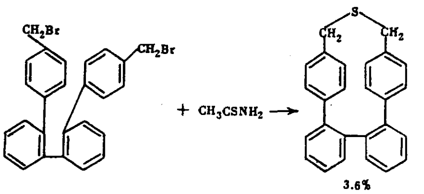
(XXIV), 12%

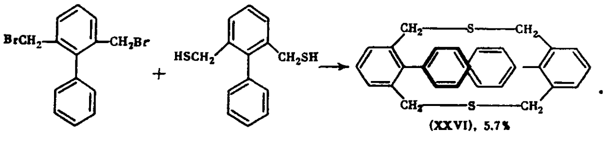


(XXV), 8%

Compound (XXIV) has been synthesised by Boekelheide and Hollings[124] and compound (XXV) by Vögtle et al.[125] Strained thiscyclophanes were synthesised subsequently[126] using the so called "caesium effect", which consists in the fact that the cyclocondensation of the dibromo-derivatives with thioacetamide or with 2,6-di-(mercaptomethyl)biphenyl takes place only in the presence of equimolecular amounts of caesium ions (in the form of Cs_2CO_3 in DMF); the yields of the required products are however low.



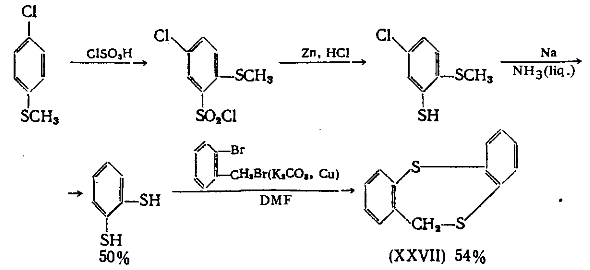




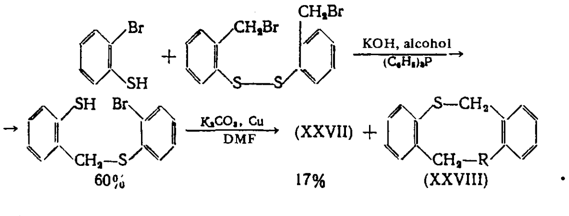
(XXVI), 5.7%

Compound (XXVI) is a mixture of the *syn*- and *anti*-stereo**isomers which are** separated by chromatography on silica gel.

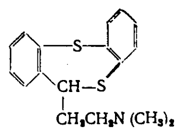
In order to obtain substances with psychotropic (antidepressant) activity, Czech investigators[127] synthesised derivatives of dithiacyclophanes—11*H*-debenzo[b,e]-1,4-dithiepin (XXVII); the starting compound was 4-chlorothioanisole:



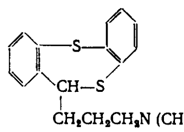
If the synthesis of compound (XXVII) was begun with 2-bromothiophenol, then another dithiacyclophane, namely 6*H*,12*H*-dibenzo[*b*,*f*]-1,5-dithiocin (XXVIII), was obtained together with compound XXVII):



By treating compound (XXVII) with butyl-lithium and 2-dimethylaminoethyl or 3-dimethylaminopropyl chloride, the dithiacyclophanes (XXIX) and (XXX) were obtained respectively (the pure compounds were obtained in the form of the oxalates); they were found to exhibit antireserpine activity:



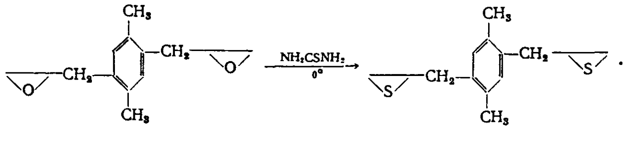
(XXIX), 97%



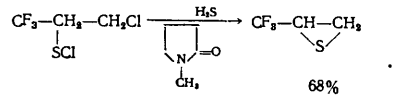
(XXX), 87%

The most important studies published during the preparation of the review for print are examined below.

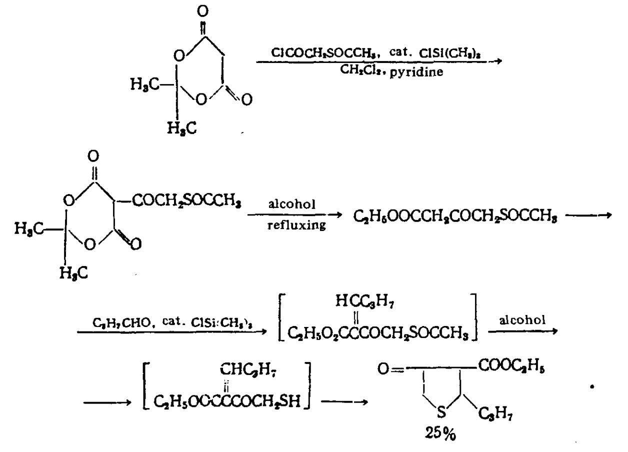
Unsubstituted acetylthiirans and 2- and 3-methylacetylthiirans have been obtained in 70–80% yields from acetyloxirans.[128] The latter are converted into diethylketals, which are treated with thiourea and then hydrolysed. The oxygen is readily replaced by sulphur in the symmetrical dioxiran:[129]



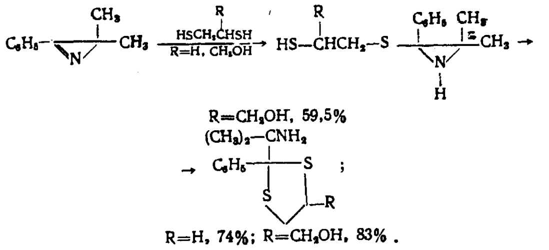
Trifluoromethylthiiran has been obtained[130] from chloropropane-2-sulphenyl chloride and hydrogen sulphide:



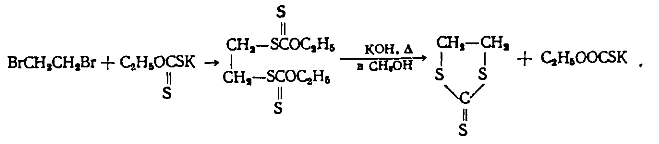
Polyfunctional derivatives of thiolan have been synthesised[131] using Meldrum's acid, for example:



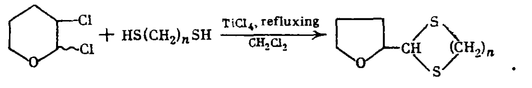
2-Aminoalkylated derivatives of 1,3-dithiolan have been synthesised from β-dithiols and 2*H*-azirines:[132]



A preparative method of synthesis of 1,3-dithiolan-2-thione and 4-phenyl-1,3-dithiolan-2-thione from dibromoethane and 1,2-dibromo-1-phenylethane and xanthate has been described:[133]

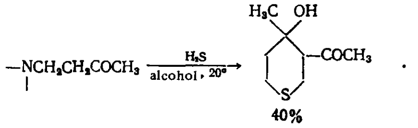


2-Tetrahydrofuryl-1,3-dithiolan and 2-tetrahydrofuryl-1,3-dithiane have been obtained[134] from dithiols and 2,3-dichlorotetrahydropyran:

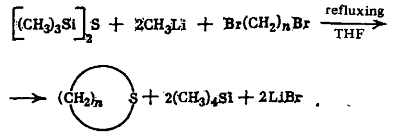


n=2–70%, n=3–73%

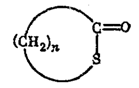
A polyfunctional thiane has been obtained by treating ketonic Mannich bases with hydrogen sulphide:[135]



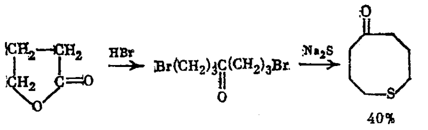
Sulphides containing more than six members in the ring have been synthesised[136] using the reactive form of Li_2S (at the instant of formation) in accordance with the scheme:



The yields in order of the number *n* were as follows (%): 6.61, 7.34, 8.22, 9.15, 10.20, and 12.31. The macrocyclic thiolactones

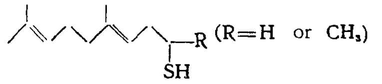


have also been obtained by reaction with $Br(CH_2)COCl$. The yields of the thiolactones in order of the number *n* were as follows (%): 5.73, 7.0, 11.47, and 15.64. 5-Cyclothiaoctanone has been synthesised[137] from γ-butyrolactone:[137]

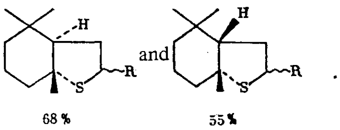


cis,cis-5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0]hexane has been synthesised[138] in 55% yield by treating specially obtained 2-thieten with tetracyanoethylene.

Cyclisation of the stereoisomers of the homogeraniolthiols

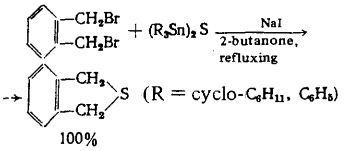


with the aid of boron trifluoride/etherate[139] the *trans*- and *cis*-*gem*-dimethyl- and the *trans*- and *cis*-trimethyl-thiahydrindans respectively; the method makes it possible to control only the stereochemistry of the ring junction:

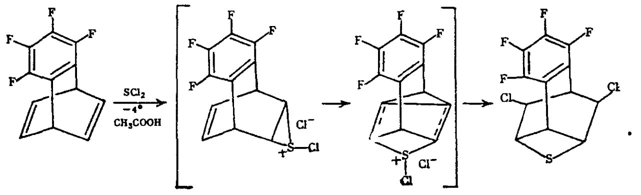


The thio-Claisen rearrangement has been extended[140] to alkenylthiotropones.

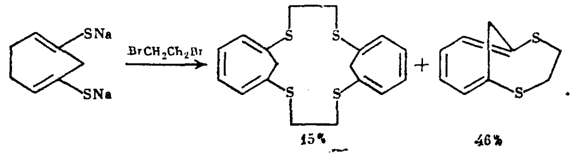
1,3-Dihydroisothionaphthene has been obtained[136] using organotin compounds:



exo-*exo* 6,9-Dichloro-3,4-tetrafluorobenzo-8-thiatricyclo-[3.3.1.0^{2,7}]nonene has been obtained[141] by means of the scheme



A thiocrown ether with a cycloheptatriene fragment has been synthesised from sodium cyclohepta-1,3,5-trienedithiolate:[142]



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Phosphorylated Allenes. Methods of Synthesis and Properties

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A systematic account is given of the literature data on the methods of synthesis of phosphorus-containing allenes. The unusual chemical behaviour of phosphorylallenes in their interaction with electrophilic addends is discussed and at the same time a new type of reaction, which leads to five-membered heterocycles containing a phosphorus atom directly in the ring, is considered. The review also deals with studies on nucleophilic addition to phosphorylallenes and
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I. INTRODUCTION

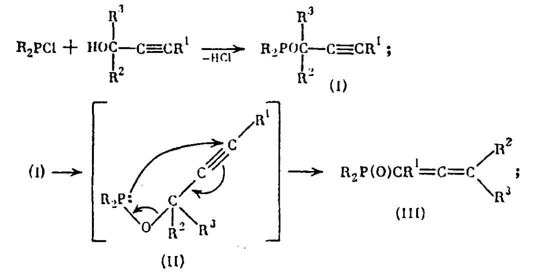
Considerable advances have been achieved in recent years in the synthesis and study of the chemical behaviour of phosphorylallenes. The enhanced reactivity of phosphorylallenes makes it possible to synthesise from them a wide variety of unsaturated organic open-chain and cyclic phosphorus compounds with functional-group substituents which are frequently difficult to obtain by other methods and which are likely to be useful as pesticides, medicinal drugs, monomers for the synthesis of plastics, etc. On the other hand, the characteristic features of the electronic structure of phosphorylallenes, in which the cumulene group with orthogonal π orbitals and different types of hybridisation of the carbon atoms (the sp^2 hybridisation of the extreme carbon atoms and the sp hybridisation of the middle carbon atoms) is combined with the electron-accepting phosphoryl group, is manifested in the physical and chemical properties of the compounds, which makes them convenient objects for the investigation of the interrelation between electronic structure, steric structure, and reactivity.

In a review of the chemistry of acetylenic and diene organophosphorus compounds (1967), mention was made of only seven allenylphosphonates;[1] since then, more than 200 phosphorus-containing allene derivatives have been synthesised. We thought it of interest and timely to survey the available information about the methods of synthesis of allene derivatives of tetracoordinate quinquevalent phosphorus. The present review also deals with certain physical characteristics of phosphorylallenes, their isomerisation, and their reactions with nucleophiles and electrophiles and derivatives of tervalent phosphorus. Studies on the 1,3-dipolar cycloaddition to phosphorylated allenes were considered earlier in other reviews.[2]

II. METHODS OF SYNTHESIS

1. The Acetylene–allene Rearrangement of Propargyl Phosphites and Phosphinites

The allene derivatives of tetracoordinate phosphorus have become available since the discovery of the acetylene–allene rearrangement of the propargyl esters of phosphorus and phosphinous acids, which are obtained from the chlorides of tervalent phosphorus acids and acetylenic alcohols in the presence of amines:[3-10]



$$R_2PCl + HOC(R^2)(R^3)-C\equiv CR^1 \xrightarrow[-HCl]{} R_2POC(R^2)(R^3)-C\equiv CR^1; \quad (I)$$

$$(I) \longrightarrow [(II)] \longrightarrow R_2P(O)CR^1=C=C(R^2)(R^3); \quad (III)$$

R=CH_3, C_6H_5, AlkO, $HC\equiv CCH_2O$, $HC\equiv CCH(C_3H_7)O$, $HC\equiv CC(CH_3)_2O$,

or $R_2 = -OCH_2CH(CH_3)O-$;

R^1=H, CH_3; R^2=R^3=H, CH_3; R^2=H, R^3=CH_3;

R^2=C_6H_5, R^3=CH_3; R^2+R^3=$(CH_2)_4$, $(CH_2)_5$.

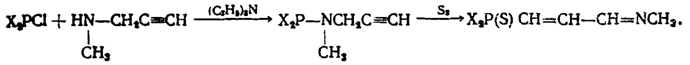
It has been suggested[3,10,11] that the rearrangement of the propargyl phosphite (phosphinite) (I) formed initially to the allenylphosphonate (III) takes place intramolecularly as an S_{ni} reaction via the five-centre cyclic transition state (II) as a result of the energy gain associated with the change in the coordination of the phosphorus atom P(III) → P(IV). The isomerisation of (I) to (II) is also regarded as a variety of the Arbuzov reaction occurring with participation of phosphorohalidites.[12]

The high stereospecificity of the acetylene–allene rearrangement, which has been confirmed experimentally in relation to the interaction of the optically pure *R*(+)-2,2,6,6-tetramethylhept-4-yn-3-ol with phosphorus trichloride, leading after hydrolysis to the optically pure *R*(−)-1,3-di-(t-butyl)-propa-1,2-dienylphosphonic acid, enabled Macomber to assume the possibility that these reactions have the mechanism involving a concerted [3,2]sigmatropic shift.[13,14]

The allenyl phosphonate (III) formed can subsequently isomerise to the corresponding acetylenic derivative (IV):[6,7]

$$\underset{(III)}{R_2P(O)CH=C=CH_2} \rightarrow \underset{(IV)}{R_2P(O)C\equiv C-CH_3}.$$

The final result of the reaction is determined by its conditions, the method of treatment of the reaction mixture, and the presence of substituents in the propargyl group.[8,10] The formation of propargyl phosphites (I) in the first stage has been confirmed by their isolation in a pure state.[8,10,15,16] It is noteworthy that, whereas propargyl phosphites and phosphorothioites[17,18] readily rearrange to allene derivatives of tetracoordinate phosphorus, their nitrogen analogues (V) are more stable:[19]

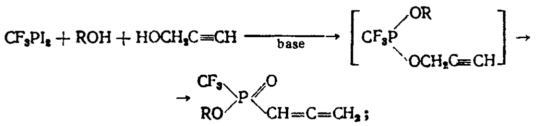


$$X_2PCl + \underset{\displaystyle CH_3}{HN}-CH_2C\equiv CH \xrightarrow{(C_2H_5)_3N} X_2P-\underset{\displaystyle CH_3}{N}CH_2C\equiv CH \xrightarrow{S_8} X_2P(S)CH=CH-CH=NCH_3.$$

(V) (VI)

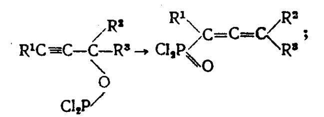
Only phosphines where X = C_2H_5 or C_6H_5 undergo the isomerisation (V) → (VI).

The rate of rearrangement of compound (I) to compound (III) depends to a large extent on the character of the substituents at the phosphorus atom and at the α-carbon atom in the propargyl group. Thus, the propargyl phosphinite (I), formed on interaction of chlorodiethylphosphine with propargyl alcohol, isomerises after several hours almost wholly with formation of an allenic phosphine oxide.[20] The propargyl esters of tervalent phosphorus acids, containing trifluoromethyl groups, also very readily isomerise to allene compounds:[21]



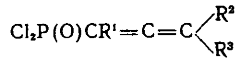
$R=C_2H_5$, $CH_2C\equiv CH$.

Like other phosphites containing the αα-disubstituted propargyl group, α-ethyl-α-methylpropargyl *o*-phenylene phosphite cannot be isolated in a pure state as a consequence of the rapid rearrangement of the corresponding phosphoryl allene.[22] The optimum condition for the rearrangement of propargyl phosphorodichloridite is ten day storage at room temperature.[16] Deuteriated propargyl phosphorodichloridite has been isomerised to the dichloride of α-deuterioallenylphosphonic acid by heating in benzene at 60–70° for 12 h.[23] Propargyl and α-methyl propargyl phosphorodichloridites isomerise to dichloroallenylphosphonates more slowly than αα-dimethylpropargyl phosphorodichloridite, whose acetylene–allene rearrangement to the chloride of 3-methylbuta-1,2-dienylphosphonic acid takes place especially readily.[12] The rate of rearrangement of acetylenic phosphorodichloridite to allenylphosphonate depends significantly on the substituents R^1, R^2, and R^3:



$R^1=H$, $R^2R^3=(CH_2)_4$ (a), $(CH_2)_5$ (b), $R^2=R^3=CH_3$ (c);
$R^1=(CH_3)_3C$, $R^2=R^3=CH_3$ (d), $R^2=H$, $R^3=(CH_3)_3C$ (e);
$R^1=R^2=R^3=H$ (f).

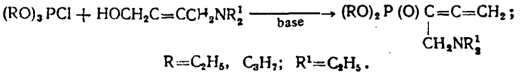
It varies in the sequence a > b > c > d > e > f.[13,14] The dichlorides of allenylphosphonic acids formed under these conditions are convenient starting materials for the synthesis of the corresponding esters,[12,14] acid difluorides,[16] and acids.[13,14,24] Dimethyl(3-methylbuta-1,2-dienyl)phosphine oxide has been obtained from the dichloride of 3-methylbuta-1,2-dienylphosphonic acid and methylmagnesium iodide.[25,26] It is noteworthy that the dichlorides of the allenylphosphonic acids



$$Cl_2P(O)CR^1=C\begin{matrix}R^2\\R^3\end{matrix}$$

can also be obtained from propargyl alcohols and phosphorus trichloride using a vigorous stream of nitrogen to remove the hydrogen chloride formed from the reaction mixture.[14] The dichlorides of allenylphosphonic acids can also be obtained by refluxing the corresponding acetylenic alcohols in an excess of phosphorus trichloride or by treating the amides of alkal-1,2-dienylphosphonic acids with hydrogen chloride.[27]

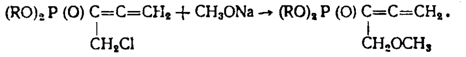
When the appropriate substituents are introduced into acetylenic alcohols, it is possible to obtain phosphorylated allenes with alkyl and aryl substituents[28–32] and also with various functional groups at the C(1) and C(3) carbon atoms of the cumulene. Thus halogenopropargyl alcohols react with halogeno-derivatives of tervalent phosphorus acids to form α-halogenoallenylphosphonates[33,34] and the corresponding phosphine oxides.[35,36] The products of the interaction of dialkyl phosphorochloridites with 4-*NN*-dialkylaminobut-2-yn-1-ols undergo thermal isomerisation with formation of dialkylaminomethyl-substituted propa-1,2-dienylphosphonates:[37]



$$(RO)_3PCl + HOCH_2C\equiv CCH_2NR^1_2 \xrightarrow[\text{base}]{} (RO)_2P(O)\underset{\displaystyle CH_2NR^1_2}{C}=C=CH_2;$$

$R=C_2H_5$, C_3H_7; $R^1=C_2H_5$.

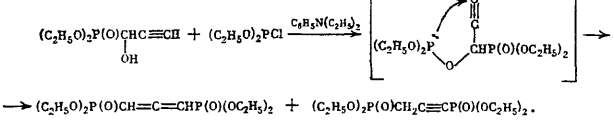
The dialkyl esters of 1-chlorobuta-2,3-dien-2-ylphosphonic acids[38] are unstable and have not been isolated in a pure state. Their formation has not been established either spectroscopically or from their chemical reactions. When sodium methoxide is introduced into the reaction mixture, chlorine is substituted by the alkoxy-group with formation of esters of 1-methoxybuta-2,3-dien-2-ylphosphonic acid:[39]



$$(RO)_2P(O)\underset{\displaystyle CH_2Cl}{C}=C=CH_2 + CH_3ONa \rightarrow (RO)_2P(O)\underset{\displaystyle CH_2OCH_3}{C}=C=CH_2.$$

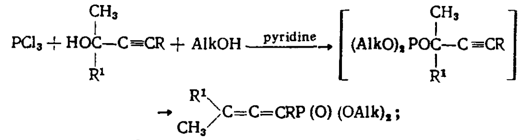
The latter have also been obtained by specific synthesis—the acetylene–allene rearrangement of the products of the interaction of 4-methoxybut-2-yn-1-ol with dialkyl phosphorochloridites.[35] The acetylene–allene isomerisation of the corresponding acetylenic phosphites, formed when the monomethyl ethers of acetylenic glycols are treated with phosphorus trichloride in the presence of pyridine, yielded the dichlorides of 1-methoxyalka-2,3-dien-2-ylphosphonic acids.[40] Dialkyl(1-methoxyalka-2,3-dien-2-yl)phosphine oxides have been synthesised by the reaction of the dichlorides of 1-methoxyalka-2,3-dien-2-ylphosphonic acids with alkylmagnesium halides.[40]

The interaction of 1-hydroxyprop-2-ynylphosphonic ester with diethyl phosphorochloridite afforded a mixture of allenic and acetylenic diphosphonates:[41]



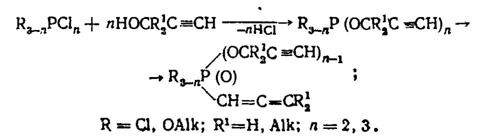
The esters of allenylphosphinothioic acids have been obtained by the isomerisation of the products of the interaction of dialkyl phosphorochloridites with acetylenethiols.[17,18]

The dialkyl esters of 1- and 3-vinylallenylphosphonic acids are formed when vinylacetylenic alcohols are treated with phosphorus trichloride and this is followed by the acetylene–allene isomerisation of the intermediate mixed phosphites;[32,33]



$R=CH=CH_2$, $R^1=CH_3$; $R=H$, $R^1=CH=CH_2$;
Alk$=CH_3$, C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9.

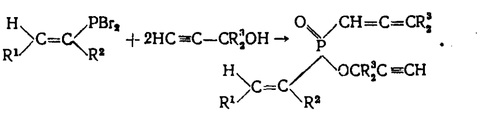
By substituting the halogen atoms in the corresponding halogeno-derivatives of tervalent phosphorus by acetylenic alcohol residues, it is possible to synthesise highly unsaturated phosphorylallenes:[3,4,42]



$$R_{3-n}PCl_n + nHOCR^1_2C\equiv CH \xrightarrow[-nHCl]{} R_{3-n}P(OCR^1_2C\equiv CH)_n \rightarrow R_{3-n}P(O)\begin{array}{l}(OCR^1_2C\equiv CH)_{n-1}\\ CH{=}C{=}CR^1_2\end{array};$$

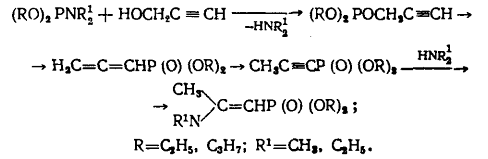
$$R = Cl,\ OAlk;\ R^1{=}H,\ Alk;\ n = 2, 3.$$

The reactions of the dibromides of alkenylphosphonous acids with acetylenic alcohols take place with rapid acetylene–allene isomerisation of the products, which leads to the monoalkynyl esters of alkenyl(allenyl)phosphinic acids:[43,44]



Alkyl allenylphosphonochloridates[44] and alkyl diethylamino-allenylphosphonates[45] have been obtained from propargyl alcohols and the corresponding tervalent phosphorus derivatives.

The alcoholysis of phosphoramidites by propargyl alcohol at 80–100 °C leads to the formation of propargyl phosphites, which immediately isomerise to allenylphosphonates and further to propynylphosphonates.[45] However, the reaction does not stop at this stage: the dialkylamine evolved adds to the triple bond of the propynylphosphonate:



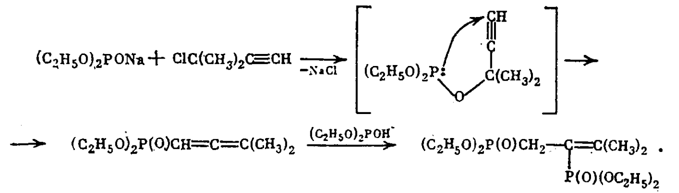
$$(RO)_2PNR^1_2 + HOCH_2C\equiv CH \xrightarrow[-HNR^1_2]{} (RO)_2POCH_2C\equiv CH \rightarrow$$

$$\rightarrow H_2C{=}C{=}CHP(O)(OR)_2 \rightarrow CH_3C\equiv CP(O)(OR)_2 \xrightarrow{HNR^1_2}$$

$$\rightarrow \begin{array}{l}CH_3\\ R^1N\end{array}\!\!>C{=}CHP(O)(OR)_2;$$

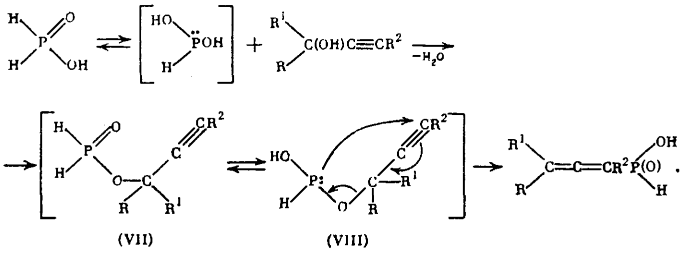
$$R{=}C_2H_5,\ C_3H_7;\ R^1{=}CH_3,\ C_2H_5.$$

The reaction of sodium diethyl phosphite with 2-chloro-2-methylbut-3-yne in ethereal solution yielded 1-diethylphosphono-3-methylbuta-1,2-diene and the product of the addition of diethylphosphorous acid to the latter:[46]



The allenylphosphonate, formed analogously in the reaction of sodium diethyl phosphite with propargyl bromide, isomerises to propynylphosphonate.[47]

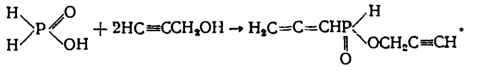
A large series of allenylphosphorous acids containing an active P–H bond have been synthesised by esterifying hypophosphorous acid with acetylenic alcohols:[48–57]



(VII) (VIII)

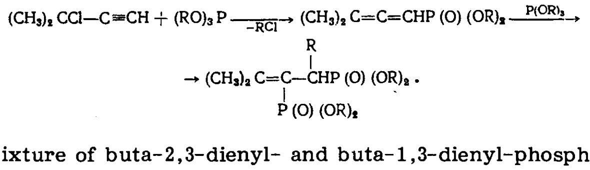
Despite the fact that the propargyl phosphite (VII) formed in the first stage contains a tetracoordinate phosphorus atom, the presence of two P–H bonds promotes the shift of the tautomeric equilibrium towards the tricoordinate form (VIII) to a larger extent than in the case of phosphite esters.[56] The high nucleophilicity of phosphorus in the intermediate (VIII) is responsible for the possibility of the acetylene–allene rearrangement.

By altering the reactant ratio, it is possible to obtain the propargyl esters of propa-1,2-dienylphosphonous acid:[52]



2. Other Methods of Synthesis of Phosphoryl Allenes

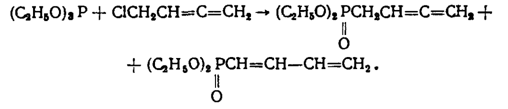
In a study of the Arbuzov reaction involving trialkyl phosphites and 2-chloro-2-methylbut-3-yne, the esters of 3-methylbuta-1,2-dienylphosphonic acid were obtained for the first time.[58] The reaction did not stop at this stage and a second molecule of the trialkyl phosphite added to the allenylphosphonate formed:



$$(CH_3)_2CCl{-}C\equiv CH + (RO)_3P \xrightarrow[-RCl]{} (CH_3)_2C{=}C{=}CHP(O)(OR)_2 \xrightarrow{P(OR)_3}$$

$$\rightarrow (CH_3)_2C{=}\underset{P(O)(OR)_2}{\underset{|}{C}}{-}\overset{R}{\overset{|}{C}}HP(O)(OR)_2.$$

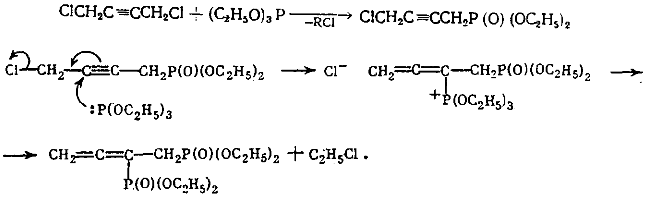
A mixture of buta-2,3-dienyl- and buta-1,3-dienyl-phosphonates is formed when triethyl phosphite reacts with 1-chlorobuta-2,3-diene:[59]



$$(C_2H_5O)_3P + ClCH_2CH{=}C{=}CH_2 \rightarrow (C_2H_5O)_2\underset{O}{\underset{\|}{P}}CH_2CH{=}C{=}CH_2 +$$

$$+ (C_2H_5O)_2\underset{O}{\underset{\|}{P}}CH{=}CH{-}CH{=}CH_2.$$

When 1,4-dichlorobut-2-yne is used, an asymmetric diphosphonate with an allene structure, namely the tetraethyl ester of buta-2,3-dien-1,2-ylenediphosphonic acid, is formed in addition to 4-chlorobut-2-ynylphosphonate:[60]



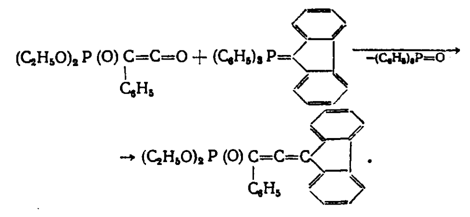
The formation of the allenediphosphonate is due to the reduced reactivity of the propargyl chloride group in 4-chlorobut-2-ynylphosphonate compared with the corresponding bromide in the Arbuzov reaction (in the latter case but-2-yn-1,4-ylenediphosphonate was obtained).

The reaction of propargyl bromide with trialkyl phosphite is of the type of Arbuzov rearrangement, being accompanied by the prototropic isomerisation of allenylphosphonate to propynylphosphonate.[61,62]

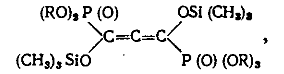
Diethyl allenylphosphonate has been obtained by the dehydrobromination of 2-bromo-1-diethylphosphonoprop-2-ene with the aid of a Grignard reagent.[63,64] The use of stronger bases (sodium alkoxide or hydride) in this reaction leads to the formation of propynylphosphonate.

C(1)- and C(3)-substituted *OO*-dimethylphosphonoallenes have been obtained in low yields in the photolysis of phosphorylvinylcarbenes.[65]

Trisubstituted phosphorylated allenes can be obtained from phosphorylketones and phosphorus ylides:[66]



A method of synthesis of 1,3-bis(dialkylphosphono)-1,3-bis-trimethylsiloxy)allenes



where R is ethyl or propyl, by the reaction of dialkyl trimethylsilyl phosphite with carbon suboxide at −30 to −70 °C,[67] has been proposed.

III. THE PROPERTIES OF PHOSPHORYLATED ALLENES

1. Structure and Physical Characteristics

Quantum-chemical calculations by the CNDO/2 method in terms of the *spd* basis set have shown that the electron density at the C(3) carbon atom increases significantly on passing from 3-alkyl-substituted to unsubstituted allenylphosphonates and -phosphonites on subsequent redistribution of the effective charges (Table 1).[68]

Table 1. Results of calculations for phosphorus-containing allenes $R^1R^2P(O)C^1H{=}C^2{=}C^3XY$ by the CNDO/2 method in terms of the *spd* basis set.[68]

R^1	R^2	X	Y	Atomic charges, a.u.				
				C(1)	C(2)	C(3)	P	=O
Cl	Cl	H	H	−0.138	0.159	−0.122	0.257	−0.252
Cl	Cl	H	CH_3	−0.139	0.134	−0.050	0.254	−0.258
Cl	Cl	CH_3	CH_3	−0.137	0,112	−0.002	0.249	−0.258
F	F	H	H	−0.162	0.160	−0.117	0 602	−0.293
CH_3O	CH_3O	H	H	−0.155	0.143	−0.123	0.453	−0.329
CH_3O	CH_3O	H	CH_3	−0.157	0.120	−0.053	0.443	−0.332
CH_3O	CH_3O	CH_3	CH_3	−0.155	0.102	−0.007	0.442	−0.334
CH_3	CH_3	CH_3	CH_3	−0.161	0.112	−0.016	0.453	−0.335
HO	HO	CH_3	CH_3	−0.165	0.114	−0.006	0.255	−0.315
HO	H	H	H	−0.166	0.173	−0.135	0.401	−0.319
HO	H	CH_3	CH_3	−0.163	0.125	−0.008	0.39	−0.325

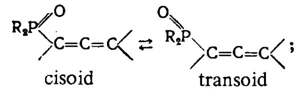
The ^{13}C chemical shift in the ^{13}C NMR spectra of phosphorylated allenes reflect the general characteristics of their structure. The signal of the *sp*-hybidised C(2) carbon atom is in the low field region (211–218 p.p.m.), while the C(1) and C(3) nuclei give rise to signals characteristic of the sp^2-hybidised atom (75–103 p.p.m.)[68] (Table 2).

The ^1H and ^{31}P NMR spectra of phosphorylated allenes have been described fairly fully in the literature[14,20,25,27,29,30,32,69,70], etc.). The chemical shift due to the phosphorus atom in the ^{31}P NMR spectra of allenylphosphonates is manifested by a signal in the range 15–20 p.p.m., shifting to the region 25–30 p.p.m. for allenylphosphine oxide and the dichlorides of allenylphosphonic acids.

Table 2. Parameters of the ^{13}C NMR spectra of allenic phosphonates and phosphinites $R^1R^2P(O)C^1R^3{=}C^2{=}C^3XY$.[68]

R^1	R^2	R^3	X	Y	Chemical shifts δ_C, p.p.m.				Spin-spin interaction constants J_{PC}, Hz			
					C(1)	C(2)	C(3)	CH_3	C(1)	C(2)	C(3)	CH_3
Cl	Cl	H	H	H	89.7	212.1	79.3	—	164,1	2.8	21.5	—
F	F	H	H	H	80.9	217.3	78.3	—	222.3	0	18.8	—
C_2H_5O	C_2H_5O	H	H	H	79.8	218.6	75.8	—	197.6	0	15.7	—
C_2H_5O	C_2H_5O	CH_3	H	H	88.7	216.0	75.7	14.2	190.1	6.4	15.4	5.0
CH_3O	CH_3O	H	H	H	77.4	215.5	96.8	19.1	195.8	3.4	16.4	6.9
Cl	Cl	H	CH_3	CH_3	89.4	209.3	103.8	18.8	162.0	4.3	24.2	9.5
CH_3	CH_3	H	CH_3	CH_3	85.4	207.8	96.5	16.1	100.4	0	13.4	6.1
HO	H	H	H	H	92.4	217.5	85.9	—	132.5	0	15.0	—
HO	H	H	CH_3	CH_3	80.8	211.3	99.8	—	193.0	0	17.0	—

The band due to the antisymmetric vibrations of the C=C=C group in the region of 1950 cm^{-1} in the IR spectra of phosphorylallenes was found to be a doublet,[16,20,71] which can be explained by the conformational isomerism arising as a consequence of the rotation relative to the $P{-}C_{sp^2}$ bond.[71] Using the set of IR and Raman spectroscopic data, dipole moments, and Kerr effect data, it has been shown that, in the liquid state and in solutions of dimethyl(3-methylbuta-1,2-dienyl)phosphine oxide and the chlorides of 3-methylbuta-1,2-dienylphosphonic and propdienylphosphonic acids, there is a conformations equilibrium between the cisoid and transoid forms, somewhat displaced towards the latter:[26]



R=CH₃, Cl.

The study of the molecular geometry for a series of allenyldiphenylphosphine oxides by ^1H NMR[29,72–76] has shown that a diamagnetic anisotropy has arisen under the influence of the aromatic nuclei attached to the phosphorus atom. Conformational analysis of these systems relative to the σ-bond between the terminal C(3) carbon atom of the phosphorylated cumulene and the substituent at this atom indicates a structure with the $C_{sp^2}{-}C_{sp^3}$ bond eclipsed by the allene system. Whether or not this orientation is preferred depends on the substituents at the C_{sp^3} carbon atom and varies in the sequence $CH_3 \gg C_6H_5 > H$.

2. Isomerisation

The isolation of esters of the 3,3-unsubstituted allenylphosphonic acid frequently presents considerable difficulties owing to the ready isomerisation to methylacetylenic phosphonates.[8] The prototropic conversion of allenylphosphonate into propynylphosphonate by treatment with propargyl phosphite, which plays the role of a basic catalyst, or in the presence of amines, alkoxides, and phosphites is accompanied by an increase of temperature and takes place quantitatively. The isomerisation of allenyldiethylphosphine oxide to the corresponding acetylenic derivative is slower compared with allenylphosphonate, which is apparently associated with the weaker electron-accepting properties of the diethylphosphine oxide group.[20]

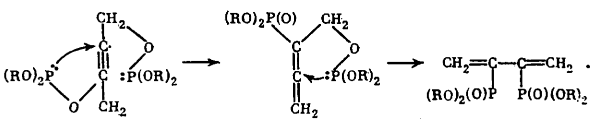
Allenylphosphonic acid dichloride and alkyl allenylphosphonochloridate do not undergo the prototropic transformation into acetylenic derivatives on heating for several hous at 100–150 °C.[34]

3-Monosubstituted allenylphosphonates are more resistant to prototropic isomerisation compared with propadienylphosphonates, which agrees with the charge distribution in phosphorylallenes[68] (Table 1). When diethylphosphonobuta-1,2-diene is heated in the presence of sodium ethoxide at 100 °C for 1.5 h, it isomerises to only a slight extent[77] and an equilibrium mixture is formed after 5 h at 160–180 °C:[78]

$$\underset{70\%}{CH_3C{\equiv}CCH_2P(O)(OC_2H_5)_2} \rightleftarrows \underset{20\%}{CH_3CH{=}C{=}CHP(O)(OC_2H_5)_2} \rightleftarrows \underset{10\%}{CH_3CH_2C{\equiv}CP(O)(OC_2H_5)_2}.$$

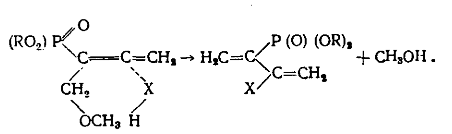
3,3-Disubstituted allenylphosphonates and allenylphosphine oxides are thermodynamically stable and do not isomerise to acetylenic derivatives.[8,78]

The allene–diene isomerisation is observed in the thermal rearrangement of diphosphites with a βγ-acetylenic bond in the common ester residue:[9]



Phosphonoprenes have been obtained by allene–diene isomerisation on distillation of relatively unstable esters of 1-chlorobuta-2,3-dien-2-ylphosphonic and 1-chloro-4-methylpenta-2,3-dien-2-ylphosphonic acids.[38,79]

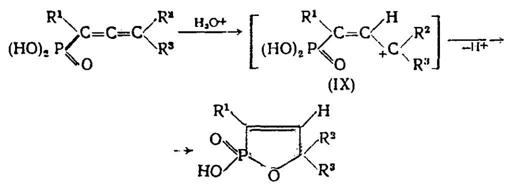
When dialkyl 1-alkoxybuta-2,3-dien-2-ylphosphonates are treated with hydrogen halides, the allene–diene isomerisation takes place with formation of esters of 3-halogenobuta-1,3-diene-2-ylphosphonic acid:[80,81]



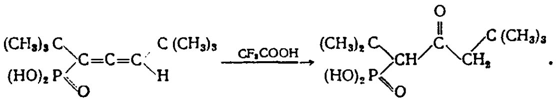
3. Electrophilic Addition

(a) Interaction of Phosphorylallenes with Proton-Donating Reagents

The reactions involving electrophilic addition to phosphorylallenes, in the course of the study of which a new reaction has been discovered, namely heterocyclisation, aroused most interest in recent years. In the study of the reactions of propargyl alcohols with phosphorus tribromide in 1971, it was observed that, when the HBr evolved is not bound by a base, then crystals of 2-bromo-3,5-di-t-butyl-2-oxo-1,2-oxa-3-phospholen are formed from 2,2,6,6-tetramethylhex-4-yn-3-ol.[82] Subsequent investigations demonstrated that the oxaphospholen is formed from phosphonoallene on treatment with proton donors.[13,14] The ease of the acid-catalysed cyclisation of allenylphosphonic acids depends to a large extent on R^2 and R^3 and to a lesser extent on R^1:



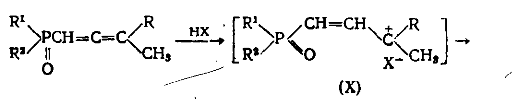
If $R^2 = R^3 = H$, then cyclisation is fully suppressed.[13] A necessary condition for cyclisation is the presence of alkyl substituents at the terminal carbon atom of phosphorylallene. The influence of substituents on the rate of cyclisation has been attributed[13] to the stability of the intermediate carbenium ion (IX), which arises in the stepwise protonation of the double bond; subsequent nucleophilic attack by the phosphoryl oxygen on the carbenium centre leads to the closure of the five-membered ring. Protophilic cyclisation proceeds as a rule regioselectively with attack by the proton on the central atom of the allene system. It might have been thought that not only Brønsted acids but also other electrophiles would promote the cyclisation of allenylphosphonic acids to the more stable oxaphospholen derivatives.[13] However, the attempt to cyclise 1,3-di-t-butylallenylphosphonic acid in trifluoroacetic acid leads to unexpected deviations,[83] which can be explained, according to the authors, by electophilic attack not on the central but on the terminal carbon atom of the allene system:



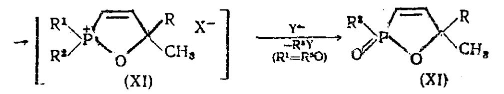
The cuases of the terminal attack by trifluoroacetic acid are not discussed in the above communication. They are most probably associated with the steric hindrance to the protonation of the central *sp*-hybridised carbon atom.

The interaction of allenylphosphonic acids with peracids leads to the formation of a mixture of products containing 4-oxo-1,2-oxaphospholan.[84]

The reactions of proton-donating electrophiles with allenylphosphonic acid esters have been fairly fully investigated.[85–89] The hydrochlorination of the dialkyl esters of 3-alkylalka-1,2-dienylphosphonic acids in polar solvents[85,86] entails cyclisation with formation of 1,2-oxaphospholens, as in the case of the allenylphosphonic acids themselves.[13,14] A general mechanism has been proposed for the cyclisation of 3,3-disubstituted allenylphosphonates in acid media, including the protonation of the central atom of the allene.[87] Subsequent attack by the internal nucleophile on the carbenium ion centre formed in the intermediate (X) leads to the cyclic quasi-phosphonium intermediate (XI) which in the case of alkoxy-substituents at the phosphorus atom is stabilised with elimination of an alkyl halide, analogously to the second stage of the Arbuzov reaction. The formation of the quasi-phosphonium intermediate (XI) in the protophilic cyclisation of phosphorylated allenes has been confirmed by the formation, in a pure state, of the crystalline quasiphosphonium salt (XI) on hydrochlorination of allenylphosphine oxide[88] for which the occurrence of a second stage of the Arbuzov reaction is impossible:



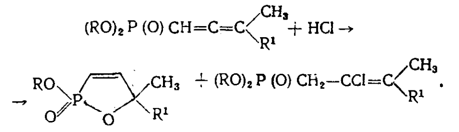
(X)



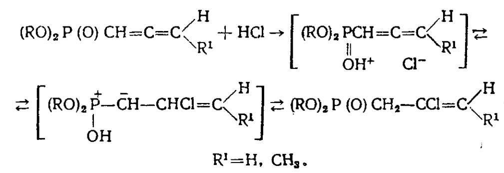
$R{=}R^1{=}R^2{=}CH_3$; $R{=}CH_3$, $R^1{=}CH_3O$, $R^2{=}C_6H_5$, CH_3O;
$R{=}CH_3$, $R^1{=}R^2{=}$iso-C_3H_7; $R{=}C_2H_5$, $R^1{=}R^2{=}CH_3O$;
$X{=}Cl^-$, HSO_4^-, CF_3COO^-;
$Y{=}Cl^-$, HSO_4^-, CF_3COO^-, HO^-, H_2O.

Kinetic study of the reactions of phosphorylallenes with aqueous solutions of sulphuric acid and anhydrous trifluoroacetic acid has shown that the protonation of the multiple bond is the slowest stage of the process considered.[87] The dependence of the rate of reaction on the acidity function of the medium and on the activation parameters indicates an appreciable degree of order in the transition state of the reaction. The acid-promoted cyclisation is an electrophilic addition reaction involving the proton and the substrate in the rate-determining stage. The protonation of the phosphoryl group slows down the reaction as a consequence of the destabilisation of the carbenium ion.

When non-polar solvents are used, products of the addition to the 1,2-double bond in allenylphosphonates are formed in the same amounts as the oxaphospholen derivatives. The yield of the 1,2-adducts reaches 80% when dimethyl sulphoxide is introduced into the reaction mixture as the aprotic ionising additive:[87]



The hydrochlorination of esters of unsubstituted allenylphosphonic acids or the acids monoalkyl-substituted at the terminal carbon atom leads to a complex mixture of open-structure compounds regardless of the polarity of the medium with the preferential formation of the products of addition to the 1,2-double bond of the allene system.[86] The authors postulate that the formation of 1,2-adducts is associated with the difficulty of stabilising the carbenium ion of type (X), which results in the competing reaction involving the nucleophilic addition of HCl:



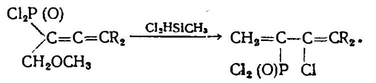
In the hydrochlorination of the dichloride of 3-methylbuta-1,2-dienylphosphonic acid, an oxaphospholen with a pentacoordinate phosphorus atom is formed slowly.[14] In the presence of aprotic ionising additives, the addition of hydrogen chloride to the dihalides of allenyl phosphonic acids leads to the formation of 1,2-adducts[89] and the introduction of alkyl substituents at the C(3) carbon atom of the cumulene system retards the reaction under these conditions. In the hydrochlorination of the dichloride of unsubstituted allenylphosphonic acid, a mixture of products of addition to the 1,2- and 2,3-double bond has been obtained:

$$Cl_2P(O)CH{=}C{=}CH_2 + HCl \rightarrow Cl_2P(O)CH_2CCl{=}CH_2 + Cl_2P(O)CH{=}CCl{-}CH_3.$$
Z and *E*

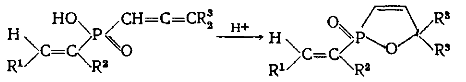
When dichloromethylsilane is used as the hydrochlorinating agent, hydrogen chloride adds to the 1,2- and 2,3-double bonds of the dichlorides of allenylphosphonic acids and a mixture of structural isomers is formed:[40]

$$Cl_2P(O)CH{=}C{=}CR_2 \xrightarrow{Cl_2HSiCH_3} Cl_2P(O)CH_2CCl{=}CR_2 + Cl_2P(O)CH{=}CCl{-}CHR_2.$$

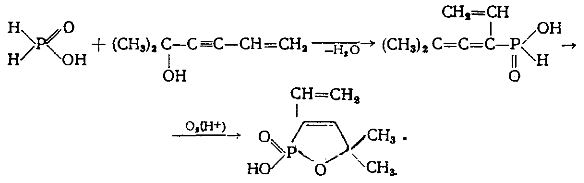
The dichlorides of 1-methoxyalka-2,3-dien-2-ylphosphonic acids react with dichloromethylsilane with the exclusive formation of the dichlorides of 3-chloroalka-1,3-dien-2-ylphosphonic acids:[40]



Highly unsaturated phosphorylallenes are converted into oxaphospholens under severe conditions (>100 °C) in the presence of inorganic acids:[44]

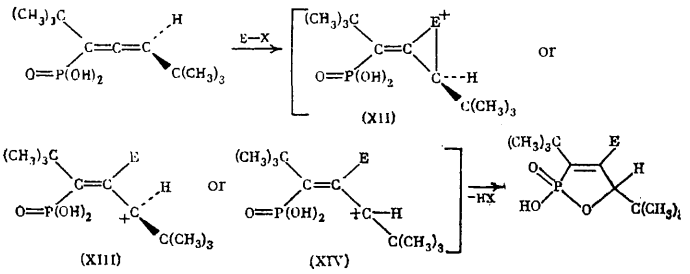


After prolonged heating of a mixture of hypophosphorous acid and Nazarov's carbinol, heterocyclisation takes place with oxidation of the P–H bond by atmospheric oxygen and the formation of 1,2-oxaphospholen:[54]



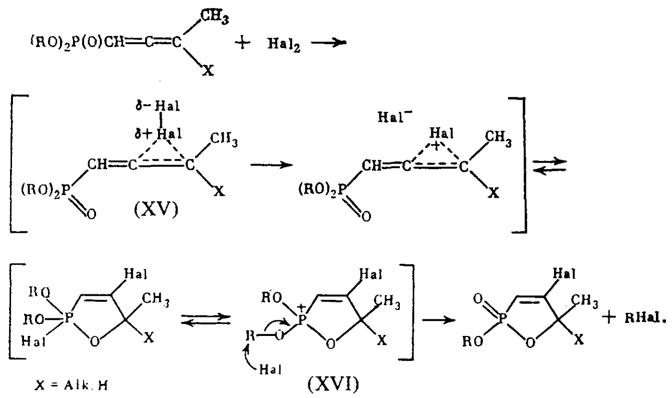
(b) The Interaction of Phosphorylated Allenes with Electrophiles Which Do not Contain a Proton

The hypothesis that phosphorylallenes are able to cyclise to 1,2-oxa-2-phospholens on treatment with not only acids but also other electrophiles[13] has been confirmed in the study of their reactions with bromine and mercury acetate. It was found that these electrophiles act more effectively than the proton-donating electrophiles. Thus 1,3-di-t-butylpropa-1,2-dienylphosphonic acid, which does not form oxaphospholens on treatment with Brønsted acids, readily cyclises on interaction with bromine or mercury acetate.[13] The stereospecificity of the interaction of electrophiles with optically active allenylphosphonic acids (81% for mercury acetate and 41% for bromine) is determined by the ability of the nucleophilic phosphoryl oxygen atom to stabilise the carbonium ion formed, which prevents racemisation. The regioselectivity of the reaction with attack by the electrophile on the central carbon atom can be accounted for by the same cause.



An intermediate in this reaction may be either the cyclic ion (XII) or the non-planar carbenium ion (XIII), which are responsible for the retention of configuration. The slight racemisation of the optically active compound may be caused by the formation of the intermediate planar allyl cation (XIV).

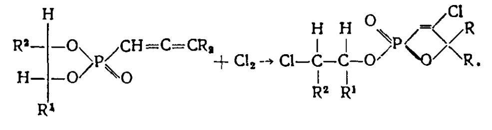
The formation of 1,2-oxa-3-phospholens is observed on interaction of bromine with allenylphosphonic acids.[90] Cyclisation takes place also when esters of 3-mono- and 3,3-di-substituted allenylphosphonic and allenylphosphinic acid are treated with halogens.[90–93] The authors[91] suggest that the π-complex or halogenium ion (XV) arising in the initial stage is converted into the cyclic quasi-phosphonium complex (XVI) as a result of the involvement of the phosphoryl oxygen:



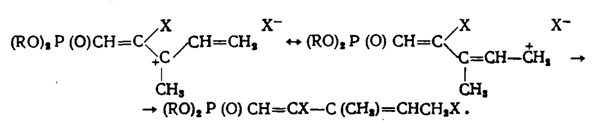
(XV) (XVI)

X = Alk, H

The authors assume that the pentacovalent structure is partly ionised and that the subsequent dissociation of the ion pair produced leads to equilibrium between tetracoordinate and pentacoordinate structures. In the case of alkoxy-groups with smaller moieties both structures are unstable and the system is stabilised by the concluding stage of the Arbuzov reaction—the elimination of the alkyl halide with formation of oxaphospholen. The rate of formation of oxaphospholens depends on the nature of the halogen and diminishes in the sequence ClI > BrI > I_2.[94] It is noteworthy that, in the interaction of allene derivatives of 1,2,3-dioxaphospholans with chlorine, the dioxaphospholan ring is cleaved and β-chloroalkoxy-1,2-oxa-3-phospholens are formed without the elimination of the alkyl chloride:[95]

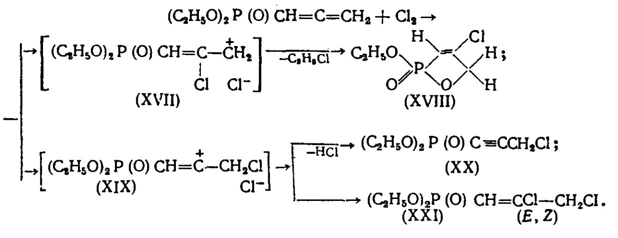


The introduction of the vinyl substituent in the 1- or 3-position in buta-1,2-dienylphosphonate does not alter the mode of interaction with halogens despite the appearance of a new reaction centre in the molecule: 3- or 5-vinyl-substituted 4-halogeno-1,2-oxa-3-phospholens are formed.[96,97] The esters of penta-1,2,4-trienylphosphonic acid afford on halogenation a small amount of 1,4-adducts together with oxaphospholens. This mode of addition has been explained by the authors by the possibility of the resonance stabilisation of the allyl cation:[97]



$(RO)_2P(O)CH{=}CX{-}C(CH_3){=}CHCH_2X$.

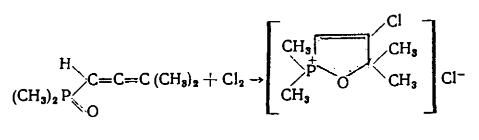
When the diethyl ester of propadienylphosphonic acid is chlorinated, a complex mixture of products is formed[92] in which it was possible to detect by NMR the oxaphospholen (XVIII), the ester of 3-chloroprop-1-ynylphosphonic acid (XX), and the ester of 2,3-dichloroprop-1-enylphosphonic acid (XXI) (the *E*- and *Z*-isomers) in the proportions (XVIII) : (XX) : (XXI) = 2 : 3 : 1. The mixture also contains a small amount of diethyl *E*-2-chloropropenylphosphonate. The formation of the ion (XIX) as an intermediate, together with the ion (XVII), leads to open-chain compounds:



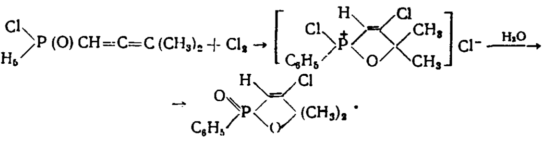
(XVII) (XVIII) (XIX) (XX) (XXI)

The introduction of electron-donating alkyl groups entails a significant difference between the energetic stabilities of the ions of the two types, which virtually rules out the formation of the intermediate (XIX).[91]

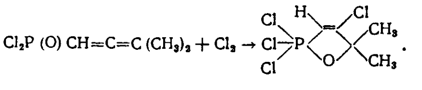
In the chlorination of buta-1,2-dienylphosphine oxides, the second stage of the Arbuzov reaction is impossible, as a result of which stable quasi-phosphonium salts are formed:[98]



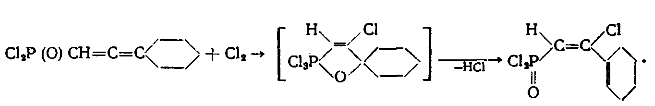
However, the chlorination of diphenylalka-1,2-dienylphosphine oxides, substituted and unsubstituted at the terminal carbon atom, leads to adducts with an open structure. The authors explained this mode of reaction by steric hindrance arising, owing the the presence of the bulky phenyl groups, in the overlap of the p-orbitals of the phosphoryl oxygen with the p orbital of the carbenium ion formed in the intermediate stage. The replacement of one phenyl group by the more electron-accepting chlorine atom leads to the formation of a ring:[98]



Cyclic phosphoranes—oxaphospholens with a pentacoordinate phosphorus atom—are formed when the chlorides of alka-1,2-dienylphosphonic acids are chlorinated:[99–102]

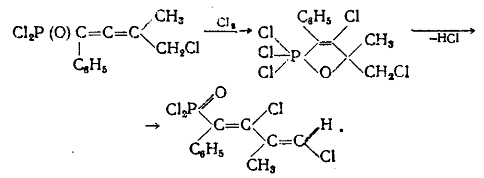


In the interaction of bromine the formation of a phosphorane cannot be observed possibly as a consequence of the more polar structure, compared with that of the phosphorane, of the bromo-derivatives of phosphorus.[100] On heating or storage, compounds of the phosphorane type split off HCl and are converted into 1,3-diene derivatives:[100–102]



The chlorination of the dichlorides of 1,3,3-trisubstituted allenylphosphonic acids also affords products with the

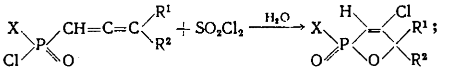
1,3-diene structure,[40,103–105] for example:



The chlorination of the dichloride of 1-t-butyl-4-chloro-3-methylbuta-1,2-dien-1-ylphosphonic acid leads to the formation of a stable quasi-phosphonium salt and the product of addition to the 2,3-double bond.[105] The stabilisation of the phosphonium salt is achieved as a consequence of the electronic and steric effects of the t-butyl group.

The interaction of chlorine with the dichloride of propyldienylphosphonic acid leads mainly to the formation of products of addition to the 2,3-double bond with an open structure.[92]

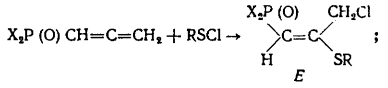
The interaction of the chlorides of 3-mono- and 3,3-disubstituted allenylphosphonic acids with sulphuryl chloride entails the formation of 1,2-oxaphospholens:[98,106]



X=Cl, C_6H_5.

A complex mixture of products of addition to one and two double bonds is formed in the chlorination of the dichloride of allenylphosphonic acid by sulphuryl chloride.[106]

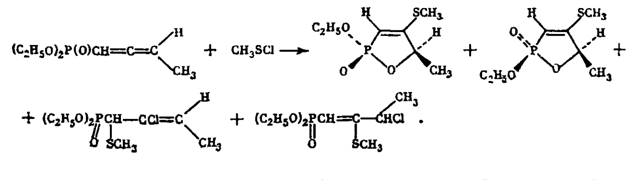
The addition of arene- and alkane-sulphenyl chlorides to the esters and dichloride of 3,3-unsubstituted allenylsulphonic acid and also to allenyldiphenylphosphine oxide takes place regioselectively and stereospecifically. Attack on the 2,3-double bonds of the cumulene takes place in the sterically more favourable *anti*-position relative to the bulky phosphoryl group located in the plane of the reacting double bond, with formation of mainly the *E*-isomer:[107–110]



X=AlkO, Cl, C_6H_5; R=C_6H_5, p-$CH_3C_6H_4$, Alk.

Similarly, selenyl chlorides form 2,3-adducts on interaction with allenylphosphonates but the *Z*-isomer predominates in the case of benzeneselenyl chloride.[111]

The introduction of alkyl substituents in the 3-position in phosphorylallene alters the mode of reaction. The ester of 3-monosubstituted allenylphosphonic acid reacts with arene- and methanesulphenyl chlorides to form diastereoisomeric oxaphospholens and also products of addition to the 1,2- and 2,3-double bonds of the cumulene in proportions of 4:1:1:1:[110]

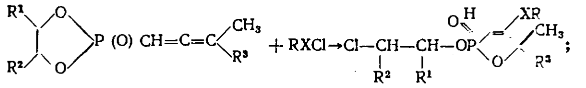


The orientation of the methylthio-group and of the chlorine atom in the 1,2-adduct has been confirmed by comparing the experimental chemical shifts of the proton at the olefinic carbon with the theoretical calculations. The diastereoisomeric oxaphospholens and products of addition to the 2,3-double bonds were not detected in the study of Angelov et al.[112] and a structure with the opposite positions of the alkylthio-group and the chlorine atom, compared with that found by Khusainova et al.,[110] was attributed to the product of addition to the 1,2-double bond.

Methaneselenyl chloride reacts with 3-monosubstituted allenylphosphonate to form an adduct at the 2,3-double bond and a small amount of a cyclic product (10%), while benzeneselenyl chloride affords exclusively the oxaphospholen.[111]

The esters of 3,3-disubstituted allenylphosphonic acids interact with alkane-, arene-,[107,113,114] and phosphonosulphenyl chlorides[110] and also with their selenium analogues[115,116] to form cyclic 4-organylthio(seleno)-1,2-oxa-3-phospholens with elimination of alkyl halides.

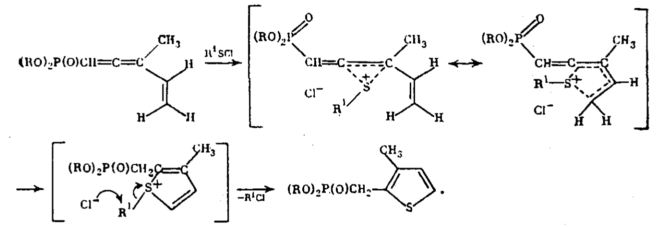
The reactions of sulphenyl and selenyl chlorides with 2-(alka-1,2-dienyl)-1,3,2-dioxaphospholan 2-oxides take place with cleavage of the dioxaphospholan ring and the formation of 1,2-oxaphospholens:[117]



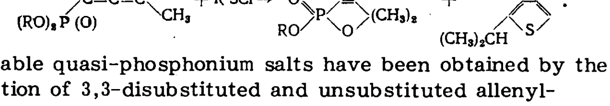
X = S or Se; R=CH_3, iso-C_3H_7; R^1, R^2, R^3=Alk.

Very small amounts of 1,2-adducts of methanesulphenyl chloride with 3-alkyl-3-methylallenylphosphonates have also been detected by column chromatography in the form of a mixture of *E*- and *Z*-isomers;[118] selenyl chloride interacts exclusively via the heterocyclisation mechanism.

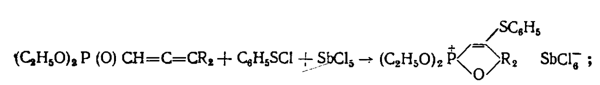
The introduction of the vinyl group into 3-methylpropa-1,2-dienylphosphonate at the C(3) carbon atom leads to the formation of phosphonylated thiophens in the reactions with alkanesulphenyl chlorides:[119]



1,3,3-Trisubstituted allenylphosphonates react with alkanesulphenyl chlorides to form 4-alkylthio-1,2-oxa-3-phospholens.[112] However, when the substituent at the C(1) carbon atom of the allene is a phenyl group, then linear products of the 2,3-addition of alkanesulphenyl chloride are formed together with oxaphospholens.[112] When the vinyl substituent is introduced into the geminal position relative to the phosphoryl group, the reaction of 1,3,3-trisubstituted phosphonoallene with alkanesulphenyl chlorides leads to the formation of a mixture of two heterocycles—thiophen and oxaphospholen:[120]

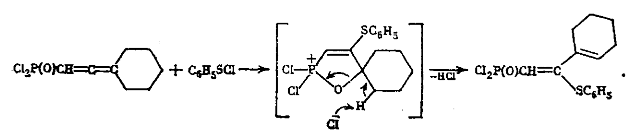


Stable quasi-phosphonium salts have been obtained by the reaction of 3,3-disubstituted and unsubstituted allenylphosphonates with benzenesulphenyl chloride in the presence of $SbCl_5$:[121]



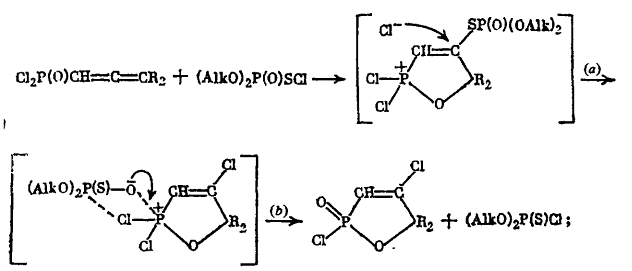
R = CH_3, H.

In contrast to esters, the dichlorides of 3,3-disubstituted allenylphosphonic acids form products with a diene structure on interaction with arenesulphenyl chlorides:[107,109]



Areneselenyl chlorides react with the dichloride of cyclohexylidenevinylphosphonic acid in the presence of SO_2 to form five-membered heterocycles.[116]

Phosphonosulphenyl chlorides react with the dichloride of 3,3-disubstituted allenylphosphonic acids to form 2,4-dichloro-oxaphospholen and the chlorides of the corresponding phosphorothioic acids, apparently via the following mechanism:[110]



$R{=}CH_3$, $R_2{=}(CH_2)_5$; Alk = CH_3, iso-C_3H_7.

Nucleophilic substitution of the "readily removed" thiophosphoryl group by the chloride anion takes place in stage (*a*). In stage (*b*) the ambident phosphorothioate anion attacks via its harder centre (the oxygen atom) the electrophilic phosphorus atom, which leads to the formation of dichloro-oxaphospholen and phosphorochloridothioate.

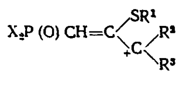
Together with the hypothesis of the formation of various open-chain and cyclic products in the reactions of phosphorylated allenes with sulphenyl chlorides, put forward as a possible explanation in a number of studies,[13,95,107] the following scheme has been discussed.[110] Four directions of attack on the allene system by the sulphenyl chloride molecule are possible in principle: at the 1,2- and 2,3-double bond in the *syn*- and *anti*-positions relative to the bulky substituent R^3 or P=O located correspondingly in the plane of the reacting double bond. Taking into account the electronic and steric factors, one can assume that there is a greater probability of attack by the sulphenyl chloride on the more nucleophilic 2,3-double bond of the phosphorylallene in the *anti*-position relative to the phosphoryl group [pathway (*a*) in the Scheme]. The nucleophilic cooperation of the phosphoryl oxygen in the attack by the sulphenyl chloride greatly facilitates the process and leads to the formation of the quasi-phosphonium intermediate (XXII). Subsequent attack by the chloride anion on the possible electrophilic centres of the quasi-phosphonium intermediate determines three main reaction pathways:

(1) If R^2, R^3 = H, then, regardless of the character of the substituents at the phosphorus atom, the attack by the chloride anion is directed to the carbon atom in the 5-position in the ring, which is the most electrophilic centre in the intermediate. This leads to intramolecular dealkylation with opening of the ring and the formation of the product of addition to the 2,3-double bond of the open-chain structure.

(2) When R^2, R^3 = Alk and X = AlkO, the attack by the chloride anion is directed to the carbon atom of the alkoxy-group and, in conformity with the second stage of the Arbuzov reaction, the quasi-phosphonium salt is dealkylated with elimination of the alkyl chloride and the formation of an oxaphospholen. When R^3 = H and X = OC_2H_5, the electrophilicities of the carbon atom of the alkoxy-group and of the C(5) atom of the intermediate are probably similar and for this reason the competing intramolecular and intermolecular dealkylation reactions take place and linear and cyclic products are formed.

(3) When R^2, R^3 = Alk and X = Cl, Alk, whereupon the second stage of the Arbuzov reaction is impossible, the attack by the chloride anion is directed to the hydrogen atom of one of the alkyl substituents in the 5-position in the ring. HCl is eliminated and products with a diene structure are formed.

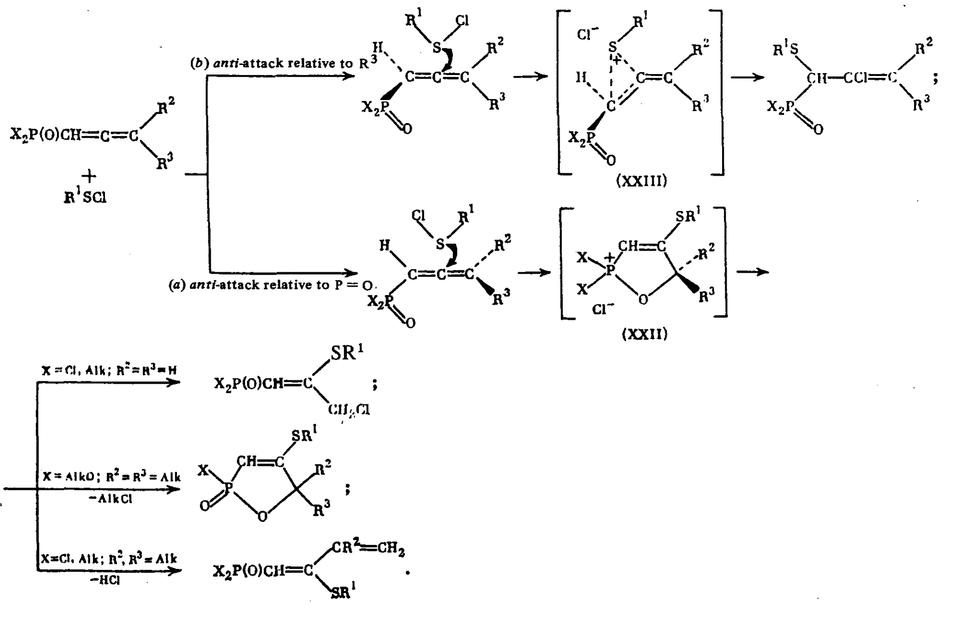
However, one cannot rule out the possibility that the formation of the 2,3-adduct and products with a diene structure is caused by the appearance of the carbenium ion



$$X_2P(O)CH{=}C(SR^1)\overset{+}{C}R^2R^3$$

and takes place by-passing the quasi-phosphonium salt (XXII) stage.[107,118]

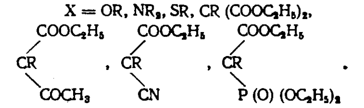
Scheme



The formation of 1,2-adducts can be accounted for solely by the attack by the sulphenyl chloride on the 1,2-double bond via pathway (*b*). According to generally accepted ideas,[122] the addition proceeds via the formation of a cyclic ion (XXIII) as an intermediate.[110,118] It may be that the addition takes place via a carbenium ion, which arises following the opening of the cyclic ion (XXIII).

4. Nucleophilic Addition to Phosphoryl Allenes

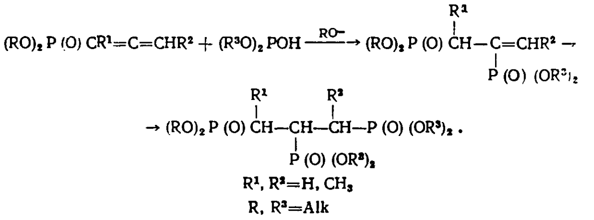
In the presence of alkali metal alkoxides, alcohols, dialkylphosphorous acids,[123,124] mercaptans,[125] and CH acids (acetoacetic and malonic esters and their homologues and cyanoacetic and phosphonoacetic esters)[125] readily add to the esters of 3,3-disubstituted allenylphosphonic acids at the 1,2-double bond activated by the electron-accepting phosphoryl group. Amines add in the absence of alkoxides also at the 1,2-double bond:[124]



$$(RO)_2P(O)CH{=}C{=}C(CH_3)_2 + XH \xrightarrow{RONa} (RO)_2P(O)CH_2{-}CX{=}C(CH_3)_2\,;$$

$$X = OR,\ NR_2,\ SR,\ CR(COOC_2H_5)_2,$$

The attack by the nucleophilic anion is directed to the central *sp*-hybridised carbon atom of the cumulene. The structure of the adducts has been demonstrated by their ozonisation, by oxidation with potassium permanganate, and by hydrolysis.[124] The degree of the addition reaction and the structure of the products formed are determined by the degree of substitution at the sp^2-hybridised carbon atoms of the allenylphosphonates. Thus only one dialkyl phosphite molecule adds to the 1,2-double bond of the esters of 3-methylbuta-1,3-dienylphosphonic acid with formation of the corresponding bisphosphonates.[124] In the case of buta-1,2-dienylphosphonic acid, small amounts of trisphosphonates are formed together with the bisphosphonates, the yield of the former increasing when esters of buta-2,3-dien-2-ylphosphonic acid are used[126]



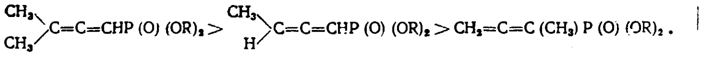
$$(RO)_2P(O)CR^1{=}C{=}CHR^2 + (R^3O)_2POH \xrightarrow{RO^-} (RO)_2P(O)\overset{\displaystyle R^1}{\overset{|}{C}}H{-}\underset{\underset{\displaystyle P(O)(OR^3)_2}{|}}{C}{=}CHR^2 \rightarrow$$

$$\rightarrow (RO)_2P(O)\overset{\displaystyle R^1}{\overset{|}{C}}H{-}\underset{\underset{\displaystyle P(O)(OR^3)_2}{|}}{C}H{-}\overset{\displaystyle R^2}{\overset{|}{C}}H{-}P(O)(OR^3)_2\,.$$

$$R^1, R^2{=}H, CH_3$$

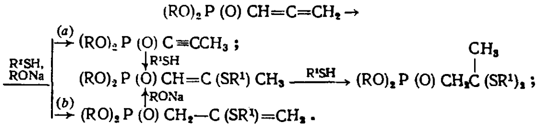
$$R, R^3{=}Alk$$

These differences can be explained by the decrease of the steric hindrance in the sequence:[126]



The esters of 3,3-unsubstituted allenylphosphonic acid combine with dialkyl phosphites to form, together with trisphosphonates, mixtures of the isomeric bisphosphonates: 1,2-bis(dialkylphosphono)prop-2-ene and 1,2-bis(dialkylphosphono)prop-1-ene.[126] Evidently, the partial prototropic allene–acetylene isomerisation of propadienylphosphonate to propynylphosphonate with the subsequent addition of the dialkyl phosphite to the triple bond leads to the formation of 1,2-bis(dialkylphosphono)prop-1-enes. ^{1}H NMR data have shown that the addition of dialkyl phosphites to 3-monosubstituted allenylphosphonates is not accompanied by the migration of the 2,3-double bond: it is retained in the adduct and the *cis*-disposition of the proton and the phosphoryl group is observed.

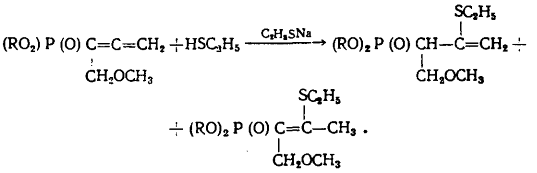
Isomerisation is likewise not observed in the addition of a mercaptan to diethyl buta-1,2-dienylphosphonates.[127] Propadienylphosphonates interact with mercaptans to form adducts with one and two addend molecules.[127] The formation of such adducts is possible also in the prototropic isomerisation of the products of addition to the 1,2-double bond of the cumulene, formed initially, to the thermodynamically more stable 1-dialkylphosphono-2-organylthioprop-1-ene [pathway (*b*)]:



$$(RO)_2P(O)CH{=}C{=}CH_2 \rightarrow$$

$$\xrightarrow[RONa]{R^1SH,}\left|\begin{array}{l} \xrightarrow{(a)} (RO)_2P(O)C{\equiv}CCH_3\,; \\ \qquad\qquad \downarrow R^1SH \\ \quad (RO)_2P(O)CH{=}C(SR^1)CH_3 \xrightarrow{R^1SH} (RO)_2P(O)CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}(SR^1)_2\,; \\ \qquad\qquad \uparrow RONa \\ \xrightarrow{(b)} (RO)_2P(O)CH_2{-}C(SR^1){=}CH_2\,. \end{array}\right.$$

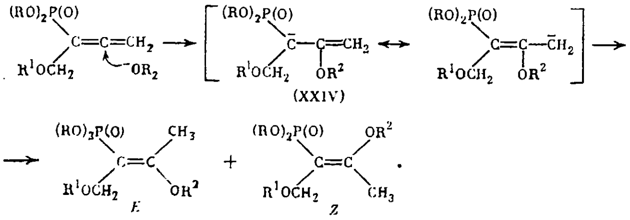
The interaction of dialkyl 1-methoxybuta-2,3-dien-2-ylphosphonates with ethanethiol in the presence of sodium mercaptide results in the formation of 3-ethylthio-1-methoxybut-3-en-2-ylphosphonates. The latter readily undergo prototropic transformations with migration of the double bond to the phosphonate group and the formation of 3-ethylthio-1-methoxybut-2-en-2-ylphosphonates:[128]



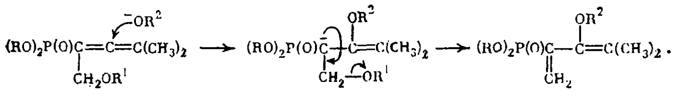
$$(RO_2)P(O)\underset{\underset{\displaystyle CH_2OCH_3}{|}}{C}{=}C{=}CH_2 + HSC_2H_5 \xrightarrow{C_2H_5SNa} (RO)_2P(O)\underset{\underset{\displaystyle CH_2OCH_3}{|}}{C}H{-}\overset{\displaystyle SC_2H_5}{\overset{|}{C}}{=}CH_2 +$$

$$+ (RO)_2P(O)\underset{\underset{\displaystyle CH_2OCH_3}{|}}{C}{=}\overset{\displaystyle SC_2H_5}{\overset{|}{C}}{-}CH_3\,.$$

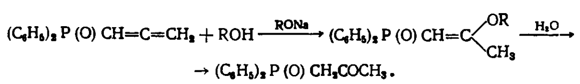
The addition of alcohols to 1-alkoxybuta-2,3-dien-2-ylphosphonates leads to the formation of the isomeric *E*- and *Z*-esters of 1,3-dialkoxybut-2-enylphosphonic acid (*E* : *Z* = 2 : 1).[39,129] Evidently, the composition of the product is determined by the thermodynamic control of the reaction with the intermediate formation of the carbanion (XXIV):



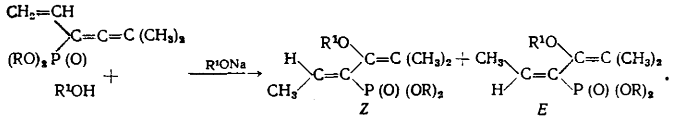
It is noteworthy that the interaction of alcohols with 1-alkoxy-4-methylpenta-2,3-dienylphosphonates results in the formation of 3-alkoxy-2-phosphonoalka-1,3-dienes:[129]



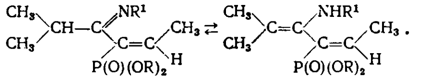
Unsubstituted phosphorylallenes combine with one alcohol molecule:[130]



3-Methyl-1-vinylbuta-1,2-dienylphosphonates readily interact with alcohols[131,132] to form 1,4-adducts, which are mixtures of the *E*- and *Z*-isomers:

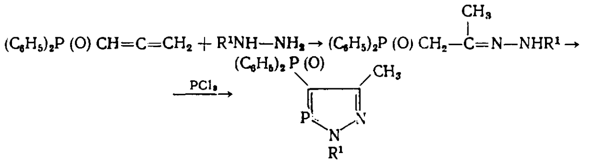


The interaction of secondary amines with 3-methyl-1-vinylbuta-1,2-dienylphosphonates also makes it possible to obtain diene phosphonates with the *trans*-disposition of the methyl and phosphoryl groups, whose formation is possible either as a result of addition to the 1,2-double bond of the allene and subsequent prototropic isomerisation or as a consequence of 1,4-addition. The use of primary amines in these reactions leads to the formation of a tautomeric mixture of imines and enamines:[133]

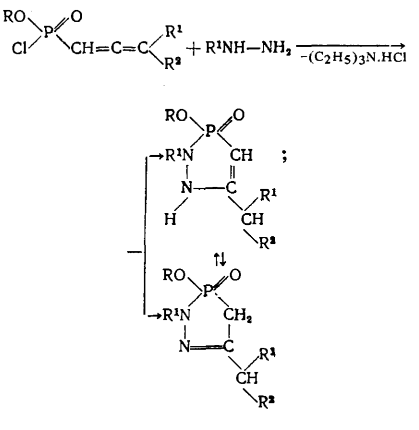


Dialkyl 1-methoxybuta-2,3-diene-2-ylphosphonates react with diethylamine to form 3-diethylaminobuta-1,3-dien-2-ylphosphonates.[134]

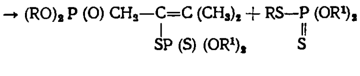
Interesting results have been obtained in the study of the interaction of phosphorylallenes with hydrazines:[130,135]



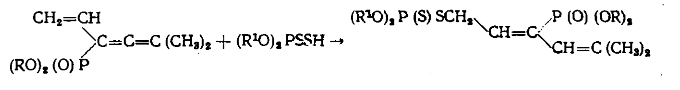
The use of the mono- and di-chlorides of allenylphosphonic acids in these reactions leads to intramolecular cyclisation:



OO-Dialkylphosphorodithioic acids interact with allenylphosphonates to form mixtures of products of addition to the 1,2-double bond of the cumulene and alkylation products—the full phosphorodithioate esters:[136]



In the reaction of 3-methyl-1-vinylbuta-1,2-dienylphosphonate the mode of addition of dialkylphosphorodithioic acids changes:[137]

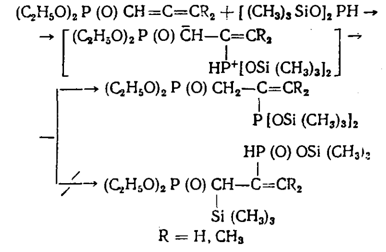


In a study of the interaction of vinylallenylphosphonates with acetylacetone, which is a CH acid, 1,2,4,5-disubstituted [tetrasubstituted? (Ed. of Translation)] benzenes were obtained unexpectedly in addition to the 1,4-adducts.

Alcohols, diethylamine,[139,140] and piperidine[141] add to the 1,2-double bond in quaternary 3-monosubstituted allenylphosphonium salts. The interaction of allylmercaptan with quaternary allenylphosphonium salts results in the formation of a mixture of products of addition to the 1,2- and 2,3-double bonds of the cumulene, which is associated with the partial prototropic isomerisation of the 1,2-adduct formed initially.[140]

5. Reactions With Derivatives of Tervalent Phosphorus

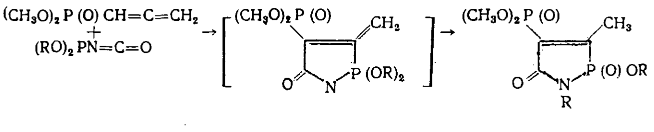
In the reaction of propa-dienyl- and 3-methylbuta-1,2-dienylphosphonates with bis(trimethylsilyl) hypophosphite the nucleophilic attack by the tricoordinate phosphorus is directed to the central carbon atom of the allene system. The intermediate dipolar ion is stabilised as a result of the migration of a proton:[142]



The prototropic isomerisation of propadienylphosphonate to propynylphosphonate is not observed under the reaction conditions.

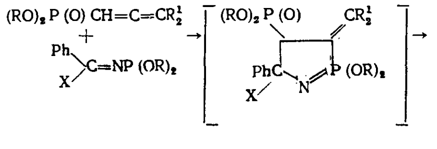
The reactions of allenylphosphonates with tervalent phosphorus derivatives containing an αβ-unsaturated fragment constitute a convenient method of synthesis of organophosphorus heterocycles.[2] The extensive experimental data which have accumulated hitherto on the reactions of these or "organophosphorus 1,3-dipoles" with alkenes and alkynes suggest that the interaction proceeds as a two-stage process and not as concerted [3 + 2]cycloaddition.

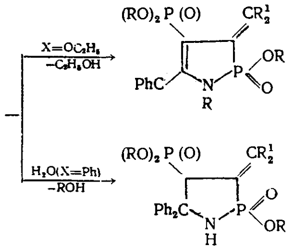
Dialkyl phosphoroisocyanatidite adds to the 1,2-double bond of allenylphosphonates:[143]



It is noteworthy that, under the cycloaddition conditions, the phosphoroisocyanatidite does not catalyse the isomerisation of allenylphosphonate to propynylphosphonate.

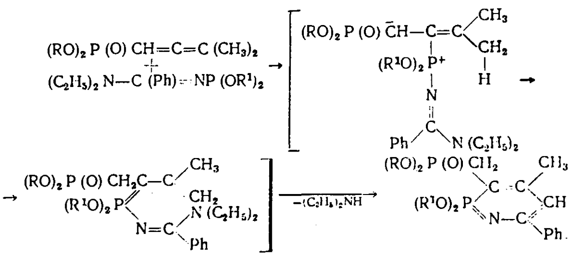
The reactions of *N*-diphenyl- and *N*-phenylethoxymethylenephosphoramidites with 3,3-disubstituted allenylphosphonates lead to the formation of the hydrolytically unstable five-membered azaphospholens with a P=N bond:[144]



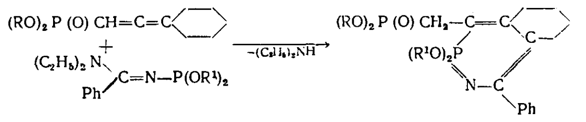


X=Ph, OC_2H_5;
$R^1=CH_3$, $R_2^1 = (CH_2)_5$

However, *N*-phenyl(diethylamino)methylenephosphoramidites give rise to stable six-membered azaphosphorines under the same conditions in accordance with the following scheme:[145]

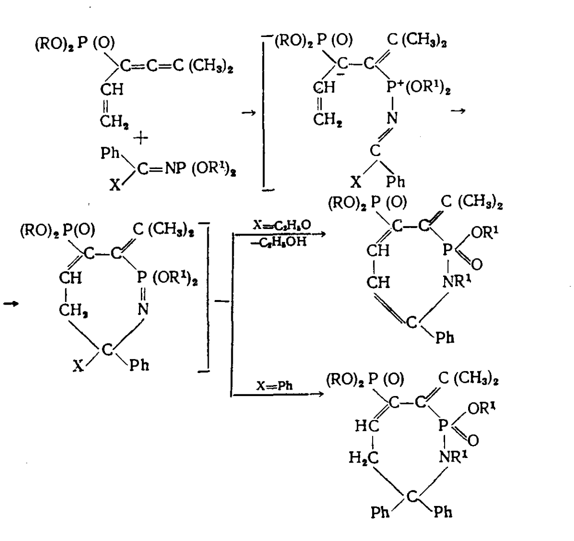


The reaction apparently begins with nucleophilic attack by the tervalent phosphorus atom on the central carbon atom of the allene system. The dipolar ion formed is stabilised by prototropic isomerisation and cyclisation with elimination of diethylamine. The interaction of cyclohexylidenevinylphosphonate with *N*-phenyl(diethylamino)methylenephosphoramidite results in the formation of a bicyclic adduct:

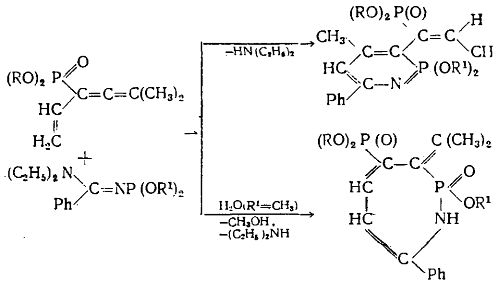


$R=CH_3$, C_2H_5, iso-C_3H_7; $R^1=CH_3$, C_2H_5

The introduction of a new reaction centre into the molecule of the 3,3-disubstituted allenylphosphonate (the vinyl group) results in the participation of the latter in the stabilisation of the intermediate dipolar ions formed in the reaction of 3-methyl-1-vinylbuta-1,2-dienylphosphonates with *N*-diphenyl- and *N*-phenyl(ethoxy)-methylenephosphoramidites:[146]



The structure of the seven-membered phosphepins was established by analysing their ^1H and ^{31}P NMR and mass-spectrometric data. 3-Methyl-1-vinylbuta-1,2-dienylphosphonates react with *N*-phenyl(diethylamino)methylenephosphoramidites to form six-membered azaphosphorines[146] similarly to 3-methylbuta-1,2-dienylphosphonates. However, this reaction pathway is not the only one: signals indicating the formation of azaphosphepines have been detected in the ^1H NMR spectrum of the reaction mixture. Crystalline azaphosphepine is the main product of the reaction of diethyl 3-methyl-1-vinylbuta-1,2-dienylphosphonate with dimethyl *N*-phenyl(diethylamino)methylenephosphoramidite:



Propadienylphosphonate does not react with *N*-methylenephosphoramidites, isomerising to propynylphosphonate in their presence.[145]

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It follows from the data examined that phosphorylated allenes can be used successfully in the synthesis of a wide variety of organophosphorus compounds. By varying the degree of substitution and the character of the substituents at the sp^2-hybridised carbon atoms of phosphoryl allenes, it is possible to activate a particular unsaturated reaction centre in the molecule. As a result of the introduction of the electron-accepting phosphoryl group into the allene molecule, the initial step of the reaction with nucleophiles is attack by the anion on the central carbon atom of the cumulene with the subsequent addition of a proton to the C(1) carbon atom. The stability of the product formed depends to a large extent on the character of the substituents at the C(3) carbon atom of the allene and on the basicity of the reacting anion, which promotes to some extent the prototropic isomerisation. The addition of electrophiles proceeds mainly at the 2,3-double bond of phosphorylallenes, also with the initial attack on the central *sp*-hybridised carbon atom, and, depending on the character of the substituents at the C(1) and C(3) atoms, leads to the formation of either products having open-chain alkene or diene structures or to heterocycles with participation of the phosphoryl group.

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Thermodynamic Compatibility of Polymers

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It is shown on the basis of an examination of studies carried out in recent years that, by a correct thermodynamically well-founded choice of polymers between which hydrogen bonds can be formed or which can give rise to electron donor-electron acceptor complexes, it is possible to create thermodynamically compatible systems; compatibility can also be improved by mixing homopolymers with copolymers. Various thermodynamic situations observed on blending polymers and the temperature dependence of their thermodynamic compatibility are discussed.

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I. INTRODUCTION

The main trend in the modern technology of the processing of polymeric materials involves their preparation from mixtures (blends) of polymers. The thermodynamic compatibility of polymers with one another, to which numerous studies surveyed in monographs, reviews, and text books have been devoted, plays a major role in this.[1-16] However, new aspects have recently arisen concerning the methods of determination of the thermodynamic compatibility of polymers, its causes, procedures for its enhancement, and its temperature dependence.

The term "compatibility", borrowed from technological practice, is usually understood as the miscibility of polymers. The authors of a monograph[2] believe that, in relation to polymer blends, the term is inept and they have suggested that it be replaced by the term "miscibility". They suggest that one can speak of miscibility only in the case of an ideal solution whose formation is possible solely following the interaction of low-molecular-weight substances. However, in essence, this is incorrect because the formation of an ideal solution is an extremely rare phenomenon and true real solutions of low-molecular-weight substances are non-ideal in the vast majority of cases.[17] Nevertheless, the concepts of "solubility" and "miscibility", which are identical, are applied to them. Evidently in the case of polymer compositions there is also no point is distinguishing these two concepts and the terms "mutual solubility" and "miscibility" should be regarded as synonymous. By thermodynamic compatibility we shall understand (a) the ability of the components to mix with one another spontaneously with formation of a true solution, i.e. their thermodynamic affinity relative to one another, and (b) a transition from possibility to reality, i.e. the realisation of the above affinity which leads to the miscibility of the components.

The thermodynamic compatibility of polymers is estimated by thermodynamic and non-thermodynamic methods. The latter include methods for the investigation of the phase structures of blends—electron microscopy and X-ray diffraction and also all the methods for the determination of the glass point of blends which yield information about the independent behaviour of the components in incompatible compositions. However, it is more correct to estimate thermodynamic compatibility by thermodynamic methods, i.e. to determine the thermodynamic affinity and phase diagrams for polymer–polymer systems.

II. THERMODYNAMIC AFFINITY BETWEEN POLYMERS

The thermodynamic affinity between a polymer and a solvent is estimated quantitatively in terms of changes in the chemical potential of the components $\Delta\mu_i$ or its excess value μ_i^e, the Gibbs free energy of mixing ΔG or its excess value G^e, the Flory–Huggins interaction parameter χ_1, and the second virial coefficient A_2.

The same parameters also characterise the thermodynamic affinity between polymers. They can be determined experimentally by studying the static and dynamic sorption of the vapour of a liquid on individual polymers and their blends, the dissolution of different polymers in a common solvent, the mutual diffusion coefficient of the polymers, etc.

The methods of the static sorption of the vapour of a common solvent was first used to estimate the thermodynamic affinity of two polymers by Kwei et al.,[18] who calculated the interaction parameter χ'_{23} from the sorption isotherm by Scott's equation:[19]

$$\ln a_1=\ln \varphi_1+(1-\varphi_1)+(\chi_{12}\varphi_2+\chi_{13}\varphi_3)(1-\varphi_1)-\chi'_{23}\varphi_2\varphi_3 \qquad (1)$$

where χ_{12} and χ_{13} are the parameters of the interaction of the polymer (2) and the polymer (3) with the common solvent (1) when the latter is sorbed on the polymer, a_1 is the activity coefficient of the solvent in the three-component polymer–polymer–solvent system, which is determined in the sorption of the vapour of the solvent on the polymer blends, and ϕ_1, ϕ_2, and ϕ_3 are the volume fractions of the solvent and the polymers (2) and (3) in the three-component composition.

It has been shown[19] that the critical value of χ'_{23} for the polymer–polymer system tends to zero. This means that any positive value of χ'_{23} characterises the incompatibility of the polymers.

Eqn.(1) has been used to estimate the compatibility of a series of systems on the basis of the sorption isotherms of the vapours of various substances.[20-22] The calculation for cellulose nitrate (CN)–poly(vinyl acetate) (PVAC) systems leads to negative values of χ'_{23}, which are consistent with data obtained by other methods and indicate the compatibility of these polymers.[21] However, negative values have also been obtained for incompatible systems. The authors suggest that Scott's equation (1), derived on the basis of the Flory–Huggins theory proposed for the model of a true solution of polymers, describes only compatible single-phase polymer systems, the theory being inapplicable to two-phase colloidal systems.

In this respect, the method involving the determination of the Gibbs free energy of mixing of polymers, proposed by Tager and co-workers,[23,24] has an undoubted advantage. The method requires no models and is based solely on the assumption that the Gibbs free energy is a function of state of the system and is independent of the path followed by the process. For this reason, the Gibbs free energy can be calculated from the thermodynamic equation

$$-\Delta g_x = \Delta G_{III} - (\omega_1 \Delta G_I + \omega_2 \Delta G_{II}), \qquad (2)$$

where Δg_x is the average Gibbs free energy of mixing of the polymers, ΔG_I, ΔG_{II}, ΔG_{III} are the Gibbs free energies of respectively 1 g of each polymer and their mixtures with the vapour of a common solvent (sorbate) having different compositions, and ω_1 and ω_2 are the weight fractions of the polymers in the polymer composition.

This method has been described in detail in original papers,[23,24] monographs, and textbooks.[2,3,16] It has been applied to polymer–oligomer[25] and polymer–polymer[26–29] systems, interpenetrating networks,[30,31] and graft[32] and block copolymers.[33–35] The physical significance of the quantities calculated by Eqn.(2) has been discussed.[35,36] For block copolymers, the quantity Δg_x reflects the work necessary to mix the blocks and is equal in magnitude but opposite in sign to the work of their separation, which has been calculated theoretically.[37,38] For polymer blends, Δg_x is an integral quantity, which depends on the chemical structure and the degree of dispersion of the system components. According to Gibbs,[39–42] any extensive thermodynamic property of a two-phase system can be regarded as the sum of three contributions: by the phase α, the phase β, and the interfacial region.

If the interface, which represents a conventional geometrical surface, is two-dimensional (has no volume), then the average Gibbs free energy of mixing, i.e. the energy per gram of the mixture, is defined by the expression

$$\Delta g_x = \Delta g_\alpha + \Delta g_\beta + \sigma S, \qquad (3)$$

where Δg_α and Δg_β are the average Gibbs free energies of mixing in each phase, σ is the surface tension, and S the specific area of the interface.

Since it is known that the interfacial tensions in polymer blends are very low,[43] the last term of Eqn.(3) does not contribute significantly to Δg_x, as shown by Kuleznev.[44]

However, for real two-phase systems the interface is not two-dimensional and has a definite thickness and volume. It is especially important to take this into account in relation to polymer systems where the thickness of the transition layer may be considerable.[3,45,46] In this case it is more correct to use Guggenheim's method,[40–42] which leads to the differential equation[36]

$$dg_x = dg_0 + \underbrace{[\sigma + (\mu_1 dc_1 + \mu_2 dc_2) h]}_{dg_s} S, \qquad (4)$$

where μ_1, μ_2, c_1, and c_2 are the chemical potentials and concentrations of the components in the transition layer, h is the thickness of the transition layer, and dg_0 the Gibbs free energy of mixing, which is independent of the degree of dispersion and is related solely to the chemical structure of the components and their affinity for one another. The second term of Eqn.(4) reflects the contribution of the structural factors, including the degree of dispersion and the volume of the transition layer. When there is a high affinity between the components and the latter are fully miscible, $S = 0$ and the second term is zero. Then $dg_x = dg_0$. In the complete absence of affinity (polymerophobic behaviour), $dg_0 = 0$ and dg_x is equal to the work of dispersion and depends on the degree of dispersion. In the intermediate cases, dg_x is given by the sum of both contributions: $dg_0 < 0$, $dg_s > 0$. The magnitude and sign of dg_x depend on the ratio of these quantities.

The method of dynamic sorption or reversed gas chromatography (RGC), which has been described in detail in books[47,48] and reviews,[49,50] is used widely to investigate the thermodynamic compatibility of polymers. In contrast to classical gas chromatography, the RGC method is used to solve the converse problem—the study of the behaviour of the stationary phase (SP) and its interaction with the mobile phase. The RGC method was applied to polymer systems for the first time by Smidsrød and Guillet.[51]

A theory of the method has been developed for ideal gas chromatography[52] on the assumption that, firstly, the Henry distribution isotherm for the sorbate between the carrier gas and the SP is linear, which is valid only for the infinitely dilute solution of the sorbate in the SP, and, secondly, that it is necessary to establish equilibrium in the sorption–desorption process, which is possible when certain conditions are maintained, but this is by no means always the case for polymeric SP. This applies particularly to polymers which exist in the vitreous state under the experimental conditions. For this reason, RGC experiments with polymeric SP are as a rule carried out at temperatures at least 50 °C above the glass point T_g of the polymer, where the latter exists in the highly elastic state.[53] However, in this case too the equilibration time may be very long as a consequence of the high viscosity of the polymer.

In the study of the compatibility of polymers, the stationary phases are polymer blends on which the vapour of a volatile liquid is sorbed. If the components of the mixed SP behave independently, then the specific retention volume is made up additively of its components;[54] if they interact with one another, then deviations are observed from the additivity of the chromatographic retention parameters.[54,55] In this case the excess Gibbs free energy G^e is calculated by the equation of Waksmundzki and Suprynowicz:

$$G^e = RT\left(\ln V_{\overline{M}} - \sum_i x_i \ln V_M\right), \qquad (5)$$

where x_i is the mole fraction of the ith component in the mixture and V_{M_i} and V_M are the molar volumes of the sorbate retained respectively by the individual components and the entire mixed phase. Eqn.(5) has been used to determine G^e for mixed liquid[55–57] and polymeric[58] SP. For mixed polymeric SP, the interaction parameter χ'_{23} and the contact energy parameter X_{23}, introduced in the new Flory–Prigogine–Patterson theory,[60–62] are also calculated from the retention volume data.[59]

The thermodynamic compatibility of many oligomer–oligomer, polymer–oligomer, and polymer–polymer pairs have been investigated by the RGC method. The results have been surveyed in a number of communications.[2,48–50,63]

The method involving the determination of the second virial coefficients A_{23}, proposed by Kratochvil and co-workers for the investigation of the compatibility of polymers,[64–66] is based on the study of the light scattering by dilute solutions of polymer blends in a common solvent with subsequent calculation of A_{23} by the equation obtained on the basis of the Stockmeyer theory. The values of A_{23} have been calculated for the polystyrene–poly(methyl methacrylate) (PS–PMMA) system and for blends of different polymethacrylates and styrene–methyl methacrylate copolymers.[64–66]

The second virial coefficients have been determined[67] for binary polymer–polymer systems with the aid of the method based on neutron scattering by dilute solutions of one polymer in another. For blends of deuteriated PMMA with statistical styrene—acrylonitrile copolymers containing 19.9 and 28.7% of acrylonitrile, $A_{23} > 0$ was obtained, which indicates the compatibility of the components. Later the same method was used to investigate blends of PS with poly(phenylene oxide) and its bromo-derivatives,[68,69] with poly(methyl vinyl ether),[70] and with polymethylstyrene[71] and also blends of PMMA with poly(vinyl chloride) (PVC) and blends of statistical copolymers of styrene and acrylonitrile.[72]

The advantage of the neutron scattering method compared with the scattering of visible light consists in the possibility of investigating components having similar refractive indices. However, the complexity of the experimental equipment and the need to use deuteriated polymers limit the wide-scale application of the method.

The mutual diffusion method[73] is based on the familiar relation between the mutual diffusion coefficient D_{mu} and the second derivative of the average Gibbs free energy or the first derivative of the chemical potential with respect to composition:

$$D_{\mathrm{mu}} = D_i^{*} \frac{\varphi_i}{RT} \frac{\mathrm{d}\mu_i}{\mathrm{d}\varphi_i} = D_i^{*} \frac{\partial^2 g}{\partial \varphi_i^2} , \tag{6}$$

where D_i^* is the self-diffusion coefficient of the ith component characterising the thermal mobility of the molecules of the component and ϕ_2 is its volume fraction. The application of this method has been described in detail in a number of communications.[74–78]

III. CAUSES OF THE COMPATIBILITY OF POLYMERS AND METHODS FOR ITS IMPROVEMENT

The data on the compatibility of polymers quoted in the literature show that polymers with similar chemical structures are not compatible. On the other hand, polymers differing in their chemical nature are compatible. The question of the causes of the compatibility of polymers and of the role of their chemical structure naturally arises. This question can be considered from the thermodynamic and molecular points of view.

A thermodynamic condition for spontaneous mixing is a negative Gibbs free energy of mixing, which represents the algebraic sum of two contributions—the enthalpy (ΔH) and entropy ($T\Delta S$) contributions:

$$\Delta G = \Delta H - T\Delta S . \tag{7}$$

The view that the change in entropy on mixing polymers plays no role predominated in the literature for a long time. It was based on calculations by Gee,[79] who took into account only the combinatorial entropy of mixing determined by the number of transpositions of unlike molecules; for a polymer—polymer system, it is indeed very low. However, there exists a non-combinatorial contribution to the entropy of mixing originating from the interaction between the components. Flory and co-workers demonstrated theoretically that this contribution can be fairly large.[80] This was confirmed experimentally for the first time by Tager and co-workers.[24,26,27]

For many compatible polymer—polymer pairs, negative values of ΔH and ΔS are observed and the thermodynamic requirements which are needed for the satisfactory compatibility of the polymers have been formulated on this basis.[11]

1. The entropy of mixing of polymers $\Delta S < 0$. This means that the macromolecules in the mixture are distributed in a more ordered manner than among similar macromolecules, i.e. jointly ordered polymer structures are formed.

2. The enthalpy of mixing of polymers $\Delta H < 0$, which is possible if the interaction energy between unlike molecules is greater than between like molecules.

3. The algebraic sum of the absolute values of ΔH and $T\Delta S$ must be negative, i.e. $|\Delta H| > |T\Delta S|$.

Patterson and Robard,[13] who demonstrated theoretically that the compatibility of polymers with high molecular weight is possible provided that $\Delta H < 0$, arrived at an analogous conclusion. They state that negative enthalpies of mixing are frequently accompanied by negative entropies of mixing and that the competition between these quantities determines the sign of ΔG, i.e. the compatibility of polymers.

Thermodynamic predictions have played a major role in the understanding of the mechanism of the compatibility of polymers and have laid the scientific foundation for the creation of new compatible compositions. Together with the thermodynamic aspect, the compatibility of polymers has been considered also from the standpoint of the interaction of the macromolecules. This has been reflected in a monograph[2] whose authors indicate two ways of improving compatibility, i.e. of creating compatible polymer—polymer systems. The first consists in joining macromolecules together via chemical bonds, which is achieved as a result of the synthesis of block copolymers and interpenetrating networks and by carrying out reactions leading to the cross-linking of the mixture components. The presence of chemical bonds prevents macrolayer formation in the mixtures even if the components are thermodynamically incompatible.

The second way of improving compatibility consists in altering the chemical structure of the blended polymers in a manner which leads to a negative Gibbs free energy of mixing, which is achieved by two procedures: (1) by mixing polymers having functional groups capable of strong interaction; (2) by modifying one of the blended polymers by altering the chemical structure of the monomer units or by copolymerisation.

1. The Mixing of Polymers Having Functional Groups

This method of improving compatibility is based on the idea that large negative values of ΔH, favouring negative values of ΔG, are possible in the presence of specific interactions between the polymers. In their monograph, Olabisi et al.[2] put forward the concept of "complementary dissimilarity", according to which the unlimited mixing of polymers is possible when the macromolecules of each contain different functional groups capable of interacting. This concept is close to the idea[81] according to which the best mutual dissolution or blending is observed in substances whose molecules contain groups with opposite functionalities and not in substances with similar structures. For example, the molecules of one component may contain only proton-donating groups and those of the other only proton-accepting groups; in the blends, hydrogen bonds arise between the components which promotes dissolution. Blending is also favoured by the situation where the molecules of one component are electron donors and those of the other contain atoms having unoccupied orbitals. In this case electron donor—electron acceptor bonds (EDA bonds) are produced. The influence of the chemical structure of polymers on their miscibility has been considered in recent years from the standpoint of this concept.

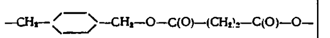
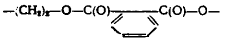
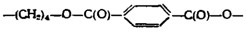
There has been a cycle of studies on the compatibility of PVC with certain polymers. The hydrogen atom in PVC, activated by the electronegative Cl atom joined to a neighbouring carbon atom, can participate in the formation of a hydrogen bond.[2,83] Consequently PVC tends to enter into donor—acceptor interactions with polymers whose molecules contain groups which function as electron donors with formation of hydrogen or EDA bonds. Poly(alkyl acrylates), poly(alkyl methacrylates), and polyesters belong to polymers of this kind. The compatibility of PVC with such polymers has been estimated from the T_g of the blends[84–90] and their transparency[84,86] and by IR spectroscopic[91–93] and DTA [differential thermal analysis] methods.[90]

It has been observed[84,94] that PVC is compatible with polyacrylates where the number of carbon atoms in the alkyl group is $n < 4$, and with polymethacrylates, where $n < 6$. The incompatibility of PVC with higher homologues has been explained by the decrease in the fraction of the $-C(O)-O$ groups in the macromolecules and by their shielding by long alkyl groups, which hinders the formation of hydrogen bonds between PVC and the ester groups of polyacrylates.

The studies considered above lead to the conclusion that PVC is compatible with PMMA, which disagrees with the data of other workers,[86,95,96] who demonstrated only their limited compatibility. The discrepancy between the results can be associated with the fact that Walsh and McKeown[84] estimated the compatibility from T_g and it is known that in the vicinity of T_g the components even in incompatible polymer systems have the same T_g.[4]

Table 1 presents data on the compatibility of PVC with polyesters. Despite the possibility of the formation of hydrogen bonds, not all the esters are compatible with PVC. The compatibility of PVC with aliphatic polyesters improves with increase in the number of CH_2 groups on passing from PBA to PCL and PHS (for the significance of the abbreviations, see Table 1), which is manifested by an increase of the negative values of the parameter χ'_{23}; when the content of CH_2 is even higher, the compatibility is impaired. It has been shown that the compatibility of aliphatic polyesters with PVC is observed in those cases where the ratio CH_x/COO ($x = 1, 2, 3$) is in the range 3 to 12.[90]

Table 1. The compatibility of PVC with polyesters.

Polyester	Designation	Structural formula	Compatibility	Refs.
Poly-β-propiolactone	PPL	$-CH_2-CH_2-C(O)-O-$	—	[92]
Poly(ethylene succinate)	PES	$-(CH_2)_2-O-C(O)-(CH_2)_2-C(O)-O-$	—	[90]
Poly(ethylene adipate)	PEA	$-(CH_2)_2-O-C(O)-(CH_2)_4-C(O)-O-$	—	[90]
Poly(2,2-dimethyl-1,3-propylene succinate)	PDPS	$-CH_2-C(CH_3)_2-CH_2-O-C(O)-(CH_2)_2-C(O)-O-$	+	[90]
Poly(butylene adipate)	PBA	$-(CH_2)_4-O-C(O)-(CH_2)_4-C(O)-O-$	+	[90]
Polyvalerolactone	PVL	$-(CH_2)_4-C(O)-O-$	+	[90, 93]
Poly-ε-caprolactone	PCL	$-(CH_2)_5-C(O)-O-$	+	[83, 85, 91]
Poly(α-ethyl-α-methyl-β-propiolactone)	PEMPL	$-CH_2-C(CH_3)(C_2H_5)-C-(O)-O-$	+	[88]
Poly(α-methyl-α-n-propyl-β-propiolactone	PMPPL	$-CH_2-C(CH_3)(C_3H_7)-C(O)-O-$	+	[88]
Poly(hexamethylene sebacate)	PHS	$-(CH_2)_6-O-C(O)-(CH_2)_8-C(O)-O-$	+	[90]
Poly(1,4-cyclohexylene-dimethyl succinate)	PCDS		+	[90]
Poly(ethylene o-phthalate)	PEOP		—	[90]
Poly(butylene terephthalate)	PBTP		+	[87]

Many studies have been devoted to the compatibility of fluorine-containing polymers with other polymers. Fluorine is the most electronegative halogen and its atom therefore forms strong chemical bonds with other atoms.[97] The strength of these bonds is the reason why many low-molecular-weight compounds containing fluorine are much less miscible with other substances and with one another than are compounds containing other halogens.[98] Thus solutions of low-molecular-weight fluorine-containing compounds are characterised by very large positive deviations from ideality and on cooling as a rule separate into layers. Fluorine-containing polymers are also inert. For example, polytetraflouroethylene does not dissolve in any known solvents.

Table 2. The compatibility of PVDF [poly(vinylidene fluoride)] with oxygen-containing polymers.

Polymer	Designation	Structural formula	Compatibility	Refs.
Poly(methyl methacrylate)	PMMA	$-CH_2-C(CH_3)-$ $C(O)-O-CH_3$	+	[101, 103, 105, 106]
Poly(ethyl methacrylate)	PEMA	$-CH_2-C(CH_3)-$ $C(O)-O-C_2H_5$	+	[101, 104]
Poly(isopropyl methacrylate)	PIPMA	$-CH_2-C(CH_3)-$ $C(O)-O-CH(CH_3)_2$	—	[101]
Poly(methyl acrylate)	PMA	$-CH_2-CH-$ $C(O)-O-CH_3$	+	[102]
Poly(ethyl acrylate)	PEA	$-CH_2-CH-$ $C(O)-O-C_2H_5$	+	[102]
Poly(isopropyl acrylate)	PIPA	$-CH_2-CH-$ $C(O)-O-CH(CH_3)_2$	—	[102]
Poly(vinyl acetate)	PVAC	$-CH_2-CH-$ $O-C(O)-CH_3$	+	[108]
Poly(vinyl propionate)	PVP	$-CH_2-CH-$ $O-C(O)-C_2H_5$	—	[108]
Poly(vinyl butyrate)	PVB	$-CH_2-CH-$ $O-C(O)-C_3H_7$	—	[108]
Poly(methyl vinyl ketone)	PMVK	$-CH_2-CH$ $C(O)-CH_3$	+	[109]
Poly(methyl vinyl ether)	PMVE	$-CH_2-CH-$ $O-CH_3$	—	[109]
Poly-ε-caprolactone	PCL	$-(CH_2)_5-C(O)-O-$	—	[109]

Poly(vinylidene fluoride) (PVDF) and fluororubber are less inert, because their molecules contain hydrogen atoms capable of forming hydrogen bonds.[97] PVDF therefore dissolves in liquids with a high electron donating capacity—dimethylformamide, dimethylsulphoxide, etc.[99] Fluororubber dissolves in acetone. These features of fluorine-containing polymers affect also their compatibility with other polymers. Thus it has been established by the RGC method that fluororubber is incompatible with ethylene–propylene rubber over a wide temperature range,[100] since hydrogen and EDA bonds cannot be formed between their macromolecules. In contrast to this, PVDF can form hydrogen bonds with oxygen-containing polymers. Numerous studies have been devoted to these blends[101–111] and their results have been surveyed[112] and are presented in Table 2. The common solvent method,[102,108,109] the method based on the determination of T_g[101,102,105,106,108,109] and T_m (melting point) of PVDF,[103,104,112] the RGC[111] and NMR[107] methods, and also the study of phase diagrams of the mixtures[110] have been used to estimate the compatibilities.

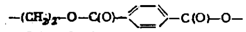
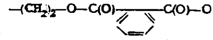
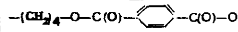
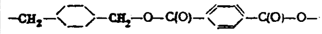
It follows from Table 2 that PVDF is compatible with polymers containing the ester group and a small alkyl substituent (CH_3, C_2H_5) in the side chain. The increase in the size of the alkyl substituent on passing to PIPMA and PIPA leads to the incompatibility of these polymers with PVDF. When the methyl group is present in the side branches, structural isomerism does not play any role: PVDF is compatible with PVAC and PMA. It is believed[109] that the presence of the carbonyl group in the molecule of the oxygen-containing polymer is of decisive importance. This follows from the fact that PVDF is compatible with PVMK and incompatible with PVME. Analysis of the interaction parameters χ'_{23} showed that PVAC, in the macromolecules of which the carbonyl group is more remote from the main chain than in the other polymers investigated, shows the maximum affinity for PVDF. In terms of increasing impairment of compatibility with PVDF, oxygen-containing polymers can be arranged in the sequence PVAC > PMMA > PMA > PEMA > PVMK > PEA. The increase in the size of the alkyl substituent impairs the compatibility of the polymers with PVDF.

It is believed[112] that the compatibility of PVDF with oxygen-containing polymers is caused by the dipole–dipole interaction between unlike molecules. However, dipole–dipole interaction alone is insufficient. Hydrogen bonds in which the carbonyl group of the ester and the hydrogen atoms of PVDF participate may be formed in these systems. This hypothesis explains the role of the carbonyl group in ensuring the greater compatibility of poly(alkyl methacrylates) with PVDF compared with poly(alkyl acrylates): the electron-donating capacity of the carbonyl group in the former is higher than in the latter as a consequence of the inductive effect caused by the presence of the methyl substituent in the α-position.[113]

Studies of the compatibility of polycarbonates (PC) based on di(hydroxyphenyl)propane with polyesters are of considerable interest:[114–120] the compatibility has been estimated by the DTA and mechanical relaxation methods. It is seen from Table 3 that the majority of the linear aliphatic polyesters obtained are compatible with PC. With increase in the number of methylene groups per carbonyl group in the polyester molecule the compatibility with PC is impaired. Branched polyesters are incompatible with PC. The replacement of aliphatic dicarboxylic acid residues in the polyester molecules by aromatic residues (PETP, PEOP) leads to their incompatibility with PC.

It is believed[120] that the compatibility of PC with polyesters is caused by the strong energetic interactions between unlike molecules, which should entail negative enthalpies of mixing. To test this hypothesis, the authors used a model approach consisting in the determination of the heats of mixing of low-molecular-weight analogues of the polymers investigated. Diphenyl carbonate (DPC), propylene carbonate, and dimethyl carbonate were adopted as models. The models for the polyesters were different esters having analogous and similar structures. It was shown[120] that low-molecular-weight esters mix with aliphatic carbonates with absorption of heat and that the sign of the heat of mixing with DPC depends on the number n of carbon atoms in the ester molecules per carbonyl group: if $n < 6$, exothermic mixing is observed ($\Delta H < 0$) and, if $n > 7$, the mixing is endothermic ($\Delta H > 0$). The authors believe[120] that the magnitude and sign of ΔH for the mixing of esters with DPC are determined by the balance of two contributions, the exothermic contribution caused by the formation of donor–acceptor bonds between the C=O group of the ester and the aromatic ring of the carbonate molecule and the endothermic contribution arising as a result of the rupture of dispersion linkages. This explanation is similar to that proposed in a study[121] of the heats of solution and swelling of aromatic polymers in tetrachloroethane and DMF. The authors[120] suggested that the positive ΔH for the model systems should correspond to the incompatibility of the polymers, while negative values should correspond to their compatibility. However, they did not observe this correlation for all systems and they reached the correct conclusion that the use of low-molecular-weight analogues to infer the compatibility of polymers is illegitimate.

Table 3. The compatibility of polycarbonate with polyesters.

Polyester	Designation	Structural formula	Compatibility	Refs.
Poly(ethylene succinate)	PES	$-(CH_2)_2-O-C(O)-(CH_2)_2-C(O)-O-$	+	[118]
Poly(ethylene adipate)	PEA	$-(CH_2)_2-O-C(O)-(CH_2)_4-C(O)-O-$	+	[118]
Poly(butylene adipate)	PBA	$-(CH_2)_4-O-C(O)-(CH_2)_4-C(O)-O-$	+	[118]
Poly-ϵ-caprolactone	PCL	$-(CH_2)_5-C(O)-O-$	+	[117]
Poly(hexamethylene sebacate)	PHS	$-(CH_2)_6-O-C(O)-(CH_2)_8-C(O)-O-$	—	[118]
Polypivalolactone	PPL	$CH_2-C(CH_3)_2-C(O)-O-$	—	[119]
Poly(2,2-dimethyl-1,3-propylene succinate)	PDPS	$-CH_2-C(CH_3)_2-CH_2-O-C(O)-(CH_2)_2-C(O)-O-$	—	[119]
Poly(ethylene terephthalate)	PETP		—	[115]
Poly(ethylene o-phthalate)	PEOP		—	[120]
Poly(butylene terephthalate)	PBTP		—	[114]
Poly(1,4-cyclohexylenedimethyl terephthalate)	PCDTP		+	[116]
Copolyester based on terephthalic acid, isophthalic acid, and 1,4-cyclohexylenedimethanol	CPL	TP + IP + CD	+	[116]

In this connection, it is appropriate to consider in a general form the relation between the thermodynamics of mixing of polymers and their liquid low-molecular-weight analogues. There is no doubt that the affinity between macromolecules of different chemical structure is related to the affinity of their monomer units. For example, CN is effectively compatible with PVA as a consequence of the high affinity of CN for vinyl acetate ($\chi_1 = 0.2$).[122] In the absence of affinity between monomer units, the polymers are undoubtedly incompatible. However, the unlimited mixing of low-molecular-weight analogues of the given polymers by no means implies that the polymers themselves are miscible.

Detailed analysis of the thermodynamic relations permits the formulation of the following rule: the higher the positive deviations from ideality in the mixtures of two liquids, i.e. the higher the excess Gibbs free energy, the less compatible the polymers whose units are analogous in structure to the molecules of these liquids. Here and henceforth the average Gibbs free energies (Δg), the enthalpies (Δh), and the entropies (Δs) of mixing of their excess values (g^e, h^e, and s^e) corresponding to the maximum in the curves relating these parameters to the composition will be used to characterise the mixing of the solution components. Thus the mixing of aromatic hydrocarbons with alkanes is accompanied by large positive deviations from ideality and the values of g^e reach 500–600 J per mole of the solution.[98] This is caused by strong $\pi-\pi'$ interaction of the aromatic rings, leading to association.[123] With increase in the size of the molecules of aromatic hydrocarbons and other aromatic compounds, the degree of association rises. For this reason, the latter do not dissolve in alkanes and are not compatible with polymeric aliphatic hydrocarbons.

Analogous behaviour has been observed in the mixing of polar liquids with non-polar liquids or of substances capable of forming hydrogen bonds with those which are not. These compounds differ sharply in the density of cohesion energy (solubility parameters) and their mixing at 298 K is accompanied by a large positive value of g^e of the order of 1000 J mol of the solution.[124] For this reason, polar polymers are incompatible with non-polar polymers over a wide temperature range.[16]

More complex rules are observed in the mixing of two polar substances or substances capable of forming hydrogen bonds. The difference between the chemical structures and not their similarity plays frequently a decisive role for these systems. We shall consider several situations.

1. The components have dissimilar chemical structures and contain only proton-accepting groups; for example, two esters. Hydrogen bonds, cannot be formed between them and their mixing is accompanied by positive values of g^e and h^e. Polymers containing ester groups as substituents are frequently altogether incompatible. The classical example is provided by the PMMA–PBMA system.[11] An improvement in compatibility can be achieved in this instance only by reducing the number of butyl substituents in the molecule of the second component, i.e. by blending PMMA with copolymers (see below).

2. The components have similar chemical structures and both contain proton-donating and proton-accepting groups: alcohol–alcohol, acid–acid, and alcohol–acid systems. In these cases, the formation of hydrogen bonds between like and unlike molecules is equally probable. For this reason, when alcohols are mixed with one another or alcohols are mixed with acids, one observes small positive values of h^e, which increase with increase in the size of the alkyl group in the molecules of alcohols or acids.[124] However, a large number of OH and COOH groups in the molecules of the mixed components promotes their blending and polymeric alcohols (PVA) are readily compatible with polyacids (PAA) with formation of polycomplexes.[125–127]

3. One component contains proton-donating and proton-accepting groups, while the other contains only proton-accepting groups. Low-molecular-weight alcohols and acids mix with esters in all proportions, but their mixing is accompanied by positive deviations from ideality. Polyacrylic acid (PAA) is infinitely miscible with poly(ethylene glycol).[127]

4. Mixing characterised by a negative value of g^e is the most favourable. It is observed in systems whose components have the opposite features: for example, one of them contains only proton-donating groups ($CHCl_3$, TCE), while the other contains only proton-accepting groups (ketones); or one is an electron donor, while the other is an electron acceptor (aromatic hydrocarbons and chloro-derivatives). Very strong hydrogen bonds or EDA complexes are formed between unlike molecules; this is accompanied by very large negative values of h^e, of the order of several thousands of J mol^{-1}, and negative deviations from ideality ($g^e > 0$). Polymers containing such groups are thermodynamically compatible for the appropriate ratios of the number of the groups and the number of hydrocarbon residues (see above).

2. Chemical Modification of the Components of a Polymer Blend

The essential feature of this method of improving compatibility consists in the alteration of the chemical structure of one of the components of the polymer composition, which leads to negative values of Δg. This is attained by replacing the units in the macromolecule of one polymer by those of the other polymer, i.e. by blending polymers with copolymers. Three cases are then observed.

In the first case, the polymer A is incompatible with the polymer B but is compatible with the polymer C. The replacement of some of the units in the macromolecule of the polymer B by those of the polymer C leads to the compatibility of the resulting copolymer with the polymer A. For example, poly(phenylene oxide) (PPO) is incompatible with poly-*p*-chlorostyrene (PPCS) but is compatible with polystyrene (PS). The compatibility of PPO with styrene–*p*-chlorostyrene copolymers of different composition has been investigated by the scanning calorimetric and mechanical relaxation methods.[128] It has been shown that the copolymers containing less than 65.3 mole % CS are compatible with PPO, while those containing more than 68% CS are incompatible. Using an improved calorimetric method, it has been shown[129] that the transition from compatibility to incompatibility occurs when the contest of CS units in the copolymer changes by less than 1% (from 67.1 to 67.8 mol %). The analogous "critical", as the authors put it, character of the compatability–incompatibility transition has been observed for mixtures of PPO with statistical styrene–*p*-fluorostyrene (PFS) copolymers:[130] PPO is compatible with copolymers containing less than 56 mol % of FS but is incompatible with copolymers with a higher FS content.

In the second case, the polymer A is incompatible with either the polymer B or the polymer C but is compatible with the copolymer BC. For example, PVC is incompatible with either polybutadiene[6] or polyacrylonitrile[131] but is compatible with their copolymer containing 40 mol % of polyacrylonitrile.[132–134] The ethylene–vinyl acetate copolymers form homogeneous mixtures with PVC, provided that their vinyl acetate content is in the range from 65 to 70 mole %.[135] An analogous "compatibility window" has been observed in the blending of PVC with butyl acrylate–acrylonitrile copolymers.[136] It has been established[137] that PMMA is compatible with the styrene–acrylonitrile copolymer containing between 9 and 27 mole % of acrylonitrile. According to other data,[138] PPO is incompatible with either PPCS or poly-*o*-chlorostyrene, but is compatible with their copolymer in the range of PS contents from 25 to 64 mole %.

Finally, an improvement of the compatibility of the polymer A with the polymer B can be achieved by replacing some of the monomer units in the macromolecule of the polymer B by those of the monomer A, i.e. by blending homopolymers with their copolymers or by blending statistical copolymers consisting of the same monomers but differing in composition. As in the previous two cases, the transition from compatibility to incompatibility occurs very sharply at a strictly defined ratio of the monomers. This has been shown in relation to the blending of statistical copolymers of different composition: styrene–acrylonitrile[139] and styrene–butadiene,[140] methyl methacrylate–butyl acrylate,[141] and butadiene–acrylonitrile.[142] It has been shown[143] that PMMA becomes incompatible with the copolymers of methyl methacrylate (MMA) with ethyl methacrylate (EMA) or butyl methacrylate (BMA) when the content of MMA in their macromolecules is less than 60%.[143]

Thermodynamic studies of the processes involving the blending of homopolymers with their copolymers[144,145] greatly expanded the existing ideas about the thermodynamics of the blending of polymers and demonstrated the possibility of the existence of several different thermodynamic situations, which are illustrated in Fig.1.

1. For strong interactions between the macromolecules of the blended polymers and for favourable steric configurations and conformations, ensuring the formation of strong ordered joint structures, negative enthalpies and entropies of mixing are observed and we have $|\Delta h| > |T\Delta s|$ and $\Delta g < 0$, i.e. the polymers are compatible over the entire composition

range. This is observed also in the blending of the polar polymers (CN–PMMA, CN–PVAC),[11,26] aromatic polymers whose macromolecules are capable of forming π-complexes,[146] and also in rubber–rubber systems.[100] In the latter case, the compatibility of the polymer is promoted by the dense joint packing of the flexible macromolecules, ensuring a strong dispersion interaction on which the π–π' interaction of the electrons of the double bonds is superimposed. The limiting case in this situation involves the formation of polycomplexes, for example the polycomplexes of polyacrylic acids with poly(vinyl alcohol) and PAA–PEO polycomplexes.[127]

Negative values of all the parameters of mixing are also observed for these systems and on the curves representing their concentration dependence there are singular points corresponding to a chemical compound with a stoichiometric component ratio (Fig.1*b*).

2. The blending of polymeric components is accompanied, as in the previous case, by a decrease of the enthalpy and entropy, but the values of $T\Delta s$ and Δh either cancel out, whereupon $\Delta g \cong 0$, or $|T\Delta s| > |\Delta h|$ and $\Delta g > 0$ (Figs.1c and 1*d*). This situation is characteristic of the blending of PVC with the copolymers of vinyl chloride (VC) and vinyl acetate (VAC),[145] containing 17.1 and 28.5 wt.% VAC, which is accompanied by the evolution of heat and a decrease of entropy as a consequence of the formation of hydrogen and EDA bonds between the macromolecules of PVC and the copolymers. However, the miscibility of PVC with these copolymers is limited and the positive Δg increase with increase of the content of VA units in the copolymer macromolecule.

3. All the thermodynamic parameters of mixing are positive (Fig.1*e*), i.e. the components are thermodynamically compatible over the entire composition range, since processes leading to the disruption of the structure, accompanied by an increase of entropy and enthalpy, predominate. A typical example of this situation is provided by the PMMA–PBMA system, for which $\partial^2 g/\partial \omega_2^2 < 0$ (ω_2 is the weight fraction of component 2), i.e. it is thermodynamically unstable.[26]

4. The compatibility of the components can be observed for positive values of Δh and Δs (Fig.1*f*). This has been noted in the blending of the oligomeric nitrile rubber SKN-40 with the ED-20 epoxy-resin.[77] The combinatorial entropy of mixing, which can be significant for oligomers, plays a role in this instance.

5. The polymeric components in one composition range are compatible ($\Delta g < 0$) while in another they are not ($\Delta g > 0$) (Fig.1*g*). Under these conditions, in the region of incompatibility ($\Delta g > 0$), the enthalpy and entropy of mixing are negative ($\Delta h < 0$ and $\Delta s < 0$), while in the region of compatibility ($\Delta g < 0$) these parameters are positive ($\Delta h > 0$ and $\Delta s > 0$). The antiparallel variation of the parameters, observed for example, for the system comprising PMMA and the copolymer of MMA and 26 wt.% BMA,[144] reflects the complexity of the processes occurring on blending the polymers, which is accompanied by the disruption of the structures of the components and the formation of new structures. The functional groups in PMMA and its copolymers are the same, but in BMA they are shielded by butyl groups. For this reason, PMMA molecules interact with one another more strongly than do the BMA units. If the copolymer macromolecules are inserted in the PMMA matrix, the energy expended on the disruption of the structure is greater than the energy gained in its interaction with PMMA. For this region, in the composition range enriched with PMMA, we have $\Delta h > 0$ and $\Delta s > 0$. Conversely, when PMMA molecules are inserted in the copolymer matrix, the energy gained is greater than the energy expended ($\Delta h < 0$ and $\Delta s < 0$). In the first case $T\Delta s > \Delta h$ and the components are compatible,

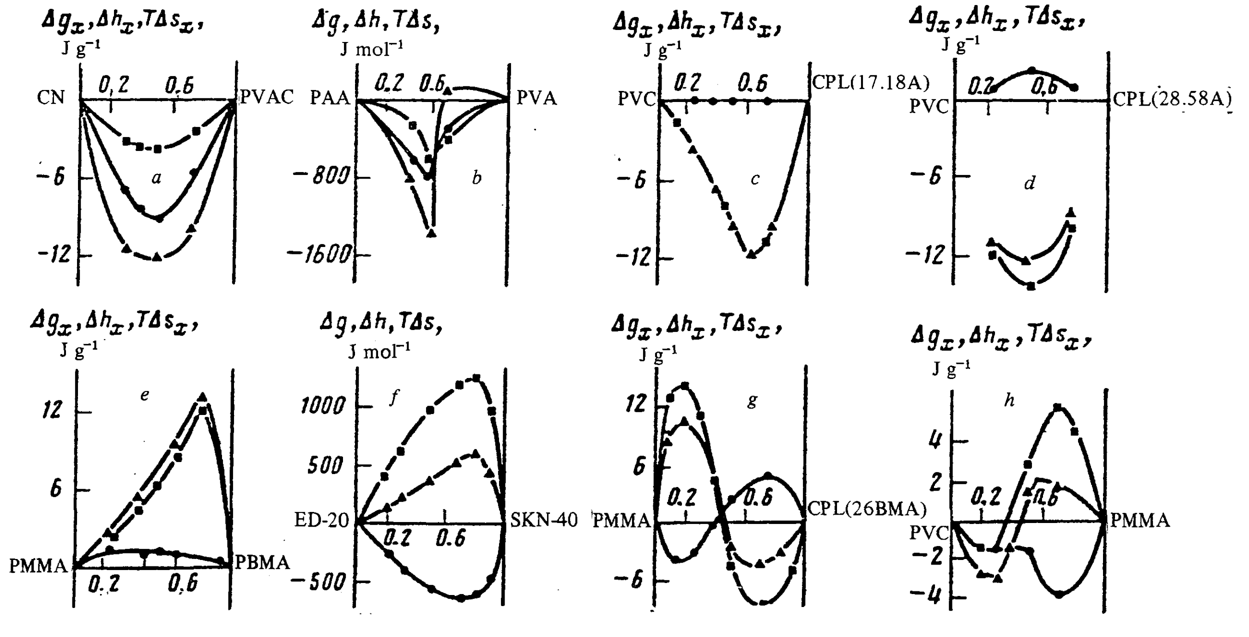


Figure 1. The possible cases of the dependence of the thermodynamic parameters of mixing on the composition of polymer blends (for the explanation, see text); the circles, triangles, and squares denote the values of Δg, Δh, and $T\Delta s$ respectively.

while in the second $|T\Delta s| > |\Delta h|$ and the blending of the components does not occur spontaneously.

It follows from Fig.1*g* that the change in the sign of Δg (transition from compatibility to incompatibility) always occurs for a component ratio which is rigorously defined for each system, i.e. a "critical" value of this ratio, since this entails a change in the ratio of Δh and $T\Delta s$. This accounts for the repeatedly observed "critical" compatibility–incompatibility transitions in homopolymer–copolymer systems.[129,139–142]

6. The enthalpy and entropy of mixing have different signs for different component ratios, as in the previous system, but the Gibbs free energy of mixing is negative over the entire composition range. On the curve for the concentration dependence of Δg_x, there is then a convex section for which $\partial^2 g/\partial\omega_2^2 < 0$ (Fig.1*h*). In this composition range, the system loses stability, but should separate into layers, which is usually observed for liquid–liquid systems.[17] However, as a consequence of the very high macroviscosity of polymer blends, layer formation does not occur and a colloidal two-phase system of this kind can exist indefinitely in a state of metastable equilibrium. This has been observed for the PVC–PMMA system[26,27] and for other similar systems.

IV. TEMPERATURE DEPENDENCE OF THE MISCIBILITY OF POLYMERS. PHASE DIAGRAMS

When the temperature is altered, single-phase binary liquid systems, including polymer solutions, undergo phase separation, which can be of the liquid–liquid type (amorphous separation) or liquid–crystal type (crystalline separation).[16,147] On the phase diagram, the boundary curve separating the homogeneous and heterogeneous regions is the binodal curve in the former case, while in the latter it is represented by the liquidus curve.

Depending on the nature of the components mixed, in amorphous phase separation binodal curves with upper and lower consolute temperatures (UCT and LCT), whose thermodynamic criteria are well known,[17] are observed. Thus for systems with UCT the excess enthalpies and entropies are positive ($h^e > 0$, $s^e > 0$) and the second derivatives of the average excess enthalpies and entropies with respect to composition are negative ($\partial^2 h/\partial\omega_2^2 < 0$, $\partial^2 s/\partial\omega_2^2 < 0$); $h^e < 0$ and $s^e < 0$ are characteristic of systems with LCT, whilst $\partial^2 h/\partial\omega_2^2 > 0$ and $\partial^2 s/\partial\omega_2^2 > 0$.

This applies fully to oligomer–oligomer and polymer–polymer systems. Consequently LCT are to be expected for systems characterised by the situations illustrated in Figs.1*a* and 1*b*, i.e. polymer blends which are compatible at the usual temperatures should separate into layers on heating. Conversely, blends characterised by endothermic mixing and positive entropies of mixing, should have UCT, i.e. the miscibility of the polymers should increase on heating. All this should be reflected in the phase diagrams, which have been obtained for many polymer compositions by various methods.

The first phase diagram for a polymer–polymer system was obtained by Allen et al.[148] by the turbidity point method or Alekseev's method.[149] Subsequently this method was used also for other polymer compositions.

The phase diagrams for oligomer–oligomer and polymer–oligomer systems have been published in a number of communications[10,12,77,78,150–157] and some of these are presented in Fig.2. They are characterised by binodal curves with UCT, limited mixing being observed even for oligomers with a very low molecular weight (MW). With increase in the MW of the components, the position of the UCT on the temperature scale changes in different ways. Thus the UCT increases steadily and the region of homogeneous mixing diminishes with increase in the MW of the components in the polydimethylsiloxane–polyisobutylene and polyethylene–polyisoprene systems (Figs.2*a* and 2*b*). The miscibility of oligomers containing end groups capable of forming hydrogen bonds (OH and others) with non-polar polymers in the region of low MW improves with increase in MW and the UCT is reduced (Figs.2*c* and 2*d*); this is associated with the decrease in the fraction of polar end groups, promoting the preferential interaction between like molecules. On further increase of MW, the end group no longer plays a decisive role and the UCT increases. In all cases at the usual temperatures, the components exhibit limited compatibility and their thermodynamic compatibility improves on heating. However, when polymers having very high molecular weights are blended, the region of homogeneous mixing is extremely small and the UCT lies in the unattainably high temperature range, i.e. does not occur in reality; this has been clearly demonstrated by Kuleznev.[3] The region of homogeneous mixing can be expanded and the UCT can be lowered by blending homopolymers with copolymers the macromolecules of which contain the residues of the same monomers. This is illustrated in Fig.3, which presents the phase diagram for poly(vinyl chloride) with vinyl chloride–vinyl acetate copolymers.[145] The figure shows that the miscibility of PVC with the vinyl chloride–vinyl acetate copolymer containing 28.5 mole % of VAC is limited. The system exhibits a wide range of heterogeneous mixing, which narrows appreciably with decrease in the number of VAC units in the copolymer macromolecule.

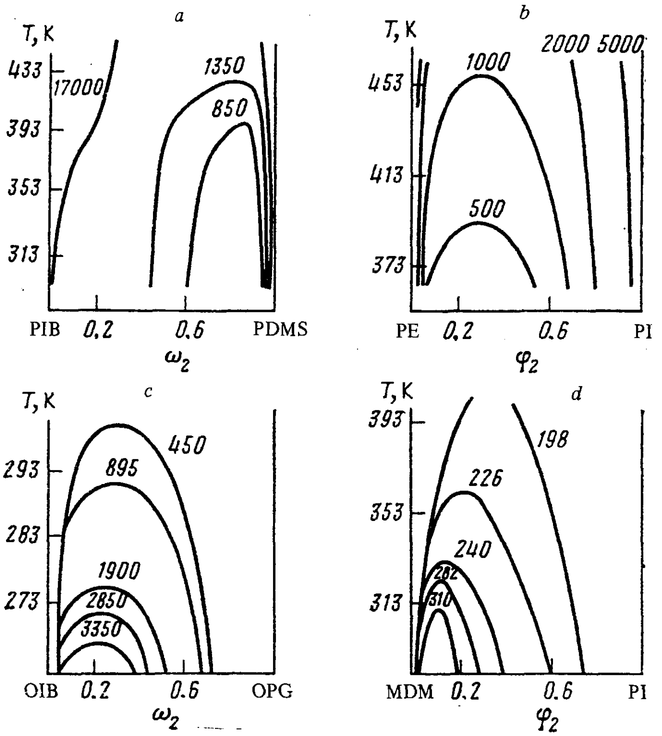


Figure 2. Phase diagrams for different systems: *a*) polyisobutylene (PIB, MW = 250)–polydimethylsiloxane (PDMS);[148] *b*) polyethylene (PE)–polyisoprene (PI, MW = 220 000);[154] *c*) oligoisobutylene (OIB, MW = 114)–oligo(propylene glycol) (OPG);[150] *d*) *p*-methylene dimethacrylate (MDM)–polyisoprene (MW = 220 000);[154] the numerals opposite the curves denote the molecular weight of the second component.

Polymers between the macromolecules where there is a possibility of specific interaction behave differently. At the usual temperatures they are miscible but their thermodynamic compatibility becomes impaired on heating and they are characterised by LCT. This was first predicted theoretically for polymer–polymer systems in two communications[8,13] and has been demonstrated experimentally for many polymer compositions (Table 4).

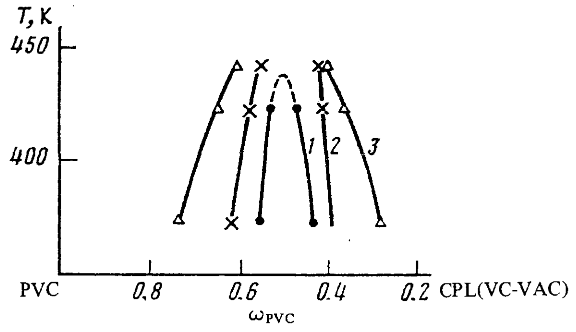


Figure 3. Phase diagram for blends of PVC with vinyl chloride–vinyl acetate copolymers containing different amounts of the latter (wt.%): *1*) 9.2; *2*) 17.1; *3*) 28.5.[145]

All that has been described above shows that the thermodynamic compatibility of polymers is promoted by the possibility of forming combined structures and by strong energetic interactions between their macromolecules. Amorphous oligomers and polymers whose macromolecules contain no functional group are incapable of specific interactions and for this reason their compatibility is as a rule limited over a wide temperature range. Their compatibility improves on heating. The compatibility of non-polar and weakly polar crystalline polymers with one another and with non-crystalline polymers is poor. Classical examples are provided by blends of polyethylene with polyisobutylene[4,134] and by blends of stereoregular rubbers—the polyisoprene and polybutadiene rubbers.[4] This can be explained by the impossibility of forming a common crystal lattice.

However, it is by no means permissible to draw from this the conclusion that the incompatibility of polymers is a rule, as has been assumed since the studies by Dobry and Boyer-Kamenoki.[172] By selecting polymers with functional groups having the opposite properties, between which there is a possibility of the formation of hydrogen bonds or electron-donor bonds, and also by reducing the size of the alkyl moieties shielding these groups, it is possible to create specifically thermodynamically stable polymer compositions, a procedure which should be followed by investigators and technologists in practice. Such compositions lose their thermodynamic stability on heating, i.e. they exhibit LCT and they must be obtained at temperatures below their LCT.

Table 4. Phase diagrams for polymer–polymer systems.

First component	M_1	Second component	M_2	Method*	Type and position of consolute temperature	Refs.
Poly(vinylidene fluoride)	88 000	poly(ethyl methacrylate)	762 000	M.T.P.	LCT; 480 K	[110]
Poly(vinylidene fluoride)	88 000	poly(methyl acrylate)	—	M.T.P.	LCT; 560 K	[110]
Poly(vinylidene fluoride)	88 000	poly(ethyl acrylate)	—	M.T.P.	LCT; 420 K	[110]
Poly-ε-caprolactone	10 000—40 000	polycarbonate	29 200	M.T.P.	LCT; 533-546 K	[110]
Poly(2,2-dimethyl-1,3-propylene succinate)	—	polyhydroxyester of bisphenol A	23 000	M.T.P.	LCT; 440 K	[158]
Poly(2,2-dimethyl-1,3-propylene adipate)	—	polyhydroxyester of bisphenol A	23 000	M.T.P.	LCT; 380 K	[158]
Poly(methyl vinyl ether)	51 500	polystyrene	10 000—200 000	M.T.P.	LCT, 370-480 K	[8,159]
Copolymer of styrene with 28% of acrylonitrile	88 600	poly(methyl methacrylate)	45 600	M.T.P.	LCT; 420 K	[160]
Copolymer of styrene with 28% of acrylonitrile	88 600	poly(ethyl methacrylate)	438 000	M.T.P.	LCT; 465 K	[161]
Copolymer of styrene with 28% of acrylonitrile	88 600	polycaprolactone	2 240	M.T.P.	LCT; 360 K	[8]
Copolymer of α-methylstyrene with 30% of acrylonitrile	57 000	poly(methyl methacrylate)	20 000—1 000 000	M.T.P.	LCT; 430-480 K	[162]
Copolymer of α-methylstyrene with 30% of acrylonitrile	57 000	poly(ethyl methacrylate)	438 000	M.T.P.	LCT; 440 K	[162]
Copolymer of *o*-chlorostyrene with 47% of *p*-chlorostyrene	220 000	poly(phenylene oxide)	17 000	D.N.P.	LCT; 550 K	[138]
Copolymer of styrene with 46% of *p*-fluorostyrene	52 000	poly(phenylene oxide)	16 900	D.N.P.	LCT; 578 K	[163]
Copolymer of acrylonitrile, butadiene, and styrene	—	poly(methyl methacrylate)	100 000	L.M.	LCT; 413 K	[164]
Polyethylene	29 000	polyisobutylene	1 800 000	L.M.	LCT; 363 K	[164]
Poly(vinyl nitrate)	—	poly(methyl methacrylate)	690 000	D.N.P.	LCT; 330 K	[165]
Chlorinated polyethylene (chlorine content 42%)	300 000	poly(vinyl chloride)	450 000	D.N.P., O.M.,E.M.	LCT; 400 K	[166]
Chlorinated polyethylene (chlorine content 27.4%)	15 200	poly(methyl methacrylate)	56 000	L.M.	UCT; 340 K; LCT, 353 K	[167]
Chlorinated polyethylene (chlorine contents 49.8 and 51.6%)	20 800—25 300	poly(methyl methacrylate)	12 200—72 800	L.M.	LCT; 370-410 K	[168]
Chlorinated polyethylene (chlorine contents 39.1 and 61.0%)	12 000	poly(methyl methacrylate)	64 000	E.-P. X.S.M.	**	[169]
Poly(vinyl chloride)	140 000	poly(methyl methacrylate)	64 000—726 000	E.-P.X.S.M.	***	[95, 156]
Poly(vinylidene fluoride)	65 000	poly(methyl methacrylate)	104 000	E.-P.X.S.M.	488 K	[170]
Copolymer of butadiene with 30% of styrene	—	*cis*-polybutadiene	—	D.N.P.	UCT; 423 K	[171]
Natural rubber	236 000	divinyl rubber	253 000	C.G.C.	LCT; 360 K	[100]
Ethylene-propylene rubber (SKEPT)	63 000	fluororubber	1 000 000	C.G.C.	UCT; 620 K	[100]

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*Designations of the methods used to determine the phase diagrams: M.T.P.—method of turbidity points; D.N.P.—determination of the number of phases in the system from T_g; L.M.—light scattering method; O.M.—optical microscopy; E.M.—electron microscopy; E.-P.X.S.M.—electron-probe X-ray spectroscopic microanalysis; C.G.C.—calculation from gas-chromatographic data.

**The solubility improves on raising the temperature; UCT above 433 K.

***The solubility improves on raising the temperature; UCT above 470 K.

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Stopped Flow and Reversed Flow Gas Chromatography

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The application of stopped flow and reversed flow gas chromatography to the study of the kinetics of slow chemical and physical processes in chromatographic column-reactors and also to the solution of a number of analytical problems is examined. It is shown that stopped flow and reversed flow gas chromatography should be regarded as a variety of headspace analysis in chromatographic column-reactors or in microreactors incorporated in a single chromatographic system.
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I. INTRODUCTION

The advances achieved recently in the study of chemical reactions in chromatographic column-reactors have been determined to a large extent by the development of methodology and experimental technique. A number of communications and chapters in monographs published in recent years have been devoted to the application of chromatographic methods to the study of the kinetics and mechanisms of reactions on the surface of an adsorbent-catalyst or in solution in the stationary phase.[1-5] However, certain recently proposed methodological procedures are either discussed too briefly and incompletely in the above communications or are not considered at all.

This review deals with the application of stopped flow gas chromatography (SFGC) and reversed flow gas chromatography (RFGC) to the study of a number of slow chemical and physical processes and also to the solution of a number of analytical problems. From our point of view, SFGC and RFGC should be regarded as a variety of the headspace analytical method,[6-8] which combines many of the modern chromatographic methods based on the gas extraction of volatile compounds from condensed liquid or solid phases.[9] Two main groups of headspace analytical methods are known:[7,8] (1) the static methods where the gas and condensed phases in contact form a closed system; (2) the dynamic methods where the phases come into contact in an open system and the gas is blown through a layer or over a layer of liquid or a granulated solid phase. In the various analytical and physicochemical applications of headspace analysis, a combination of the static and dynamic versions is frequently employed and contact between the phases is usually achieved in autonomous vessels having a constant volume (flask, bottle) or a variable volume (syringe), which are not elements of a single gas circuit of the chromatograph. The specificity of the SFGC and RFGC methods consists in the fact that the gas extraction of volatile organic compounds from stationary solid or liquid phases takes place directly in the chromatographic column-reactors or in microreactors incorporated in a single chromatographic system.

II. STOPPED FLOW GAS CHROMATOGRAPHY

The gas-chromatographic method for the study of sorption processes and chemical reactions with periodic arrests of the carrier gas flow was proposed in 1967 by Phillips and co-workers.[10-12] A fairly rigorous theory of the method, dealing with the set of diffusion, sorption, and desorption phenomena and also with chemical reactions at the active centres of the adsorbent-catalyst and the distribution of the reactant and products between the stationary and mobile phases under equilibrium and non-equilibrium SFGC conditions, was developed by Katsanos and co-workers.[13-15] The method has been described briefly in a number of communications.[1-4]

Phillips and co-workers[10-12] gave the name stopped flow chromatography to the proposed method which has now been firmly established in the English language literature (the term "stop-flow chromatography" is sometimes encountered). It is in keeping with the term "stop-flow spectrophotometry", known in Russian as "metod ostanovlennoi strui".[16] However, the stopped flow method has been developed for spectrophotometric studies of very rapid chemical reactions and is based on completely different principles and it is thereform illegitimate to employ the phrase "gazokhromatogoraficheskii metod ostanovlennoi strui" as the Russian translation of the term "stopped-flow chromatography" (see the Russian resume in Lycourghiotis's paper[17]).†

In the early analytical gas chromatographic practice, arrests of the carrier gas flow were employed in connection with the application of combined separation and detection methods even before the introduction of SFGC but for quite different purposes. This concerns the "interrupted gas chromatographic" method in which provision is made for the arrest of the carrier gas flow every time when the compound eluted from the separating column enters the cell of an insufficiently rapidly responding detector or in the combustion tube for the measurement of the IR or mass spectra, the measurement of radioactivity, or elemental analysis.[18-23] We may note that many schemes proposed[18-23] for gas circuits can be used successfully also in SFGC. Certain versions of these schemes will be considered below.

1. Principles and Applications of the SFGC Method

The traditional eluent gas chromatography is based on the continuous extraction of the compounds to be determined by the carrier gas from the stationary liquid or solid phases. The method has been used successfully for the solution of numerous analytical problems and for the physicochemical

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†The Russians use a phrase which can be translated as "gas chromatographic method with arrests of the carrier gas flow" (Ed. of Translation).

study of the processes occurring in the chromatographic column-reactors at sufficiently high rates. If a slow physical or chemical process with evolution of a volatile compound into the gas phase takes place in the column, then the chromatographic output curve for reaction systems characterised by strong retention of the reactants and weak retention of the reaction products, under the conditions of a traditional eluent gas chromatography, has the form illustrated in Fig. 1*a*. The asymmetry of the product peak is in this case due to the fact that the rate of the process investigated is lower than the rate of extraction:

$$k_r \ll k_e, \qquad (1)$$

where k_r is the reaction rate constant and k_e the extraction rate constant.

When the flow of carrier gas is stopped for a fixed time Δt, the dynamic gas extraction regime is transformed into a static regime. The volatile organic substances evolved from the stationary phase accumulate in a limited volume in the mobile phase in an amount sufficient for their detection in the form of narrow and symmetrical peaks (Fig. 1*b*) when the gas flow is subsequently restarted. The virtually identical degrees of spreading of the product bands after different arrests facilitates their identification in those cases where the impurities present in the reagent are eluted from the column. The procedure involving the repeated and consecutive stopping and restarting of the carrier gas flow for a rigorously fixed period (as a rule 1–2 min) makes it possible to measure the change in the concentration in substance B as a function of time. This distinguishes the present method from the majority of others in which the concentrations of the reactant or product thermselves are measured and not their changes.

An important advantage of the method consists in the possibility of using it to investigate reactions which lead to several products. If, for example, not one but two products are formed, traditional eluent chromatography can only indicate their formation (the break in the chromatographic output curve in Fig. 2*a*), while with the aid of SFGC it is possible to follow the changes in the ratio of the product concentrations as a function of time (Fig. 2*b*), to investigate the multistage process mechanism, and to obtain information about the comparative activities of the catalysts.

A distinctive feature of the SFGC method is the possibility of following in one experiment the course of the chemical reaction over a wide range of reactant conversions starting from very low and continuing up to very high (99.5%) degrees of conversion.[11]

At the present time many slow physical processes and chemical reactions in chromatographic column-reactors have become the objects of systematic study with the aid of SFGC: dehydration of alcohols,[11,12,17,24,25] dehydrohalogenation of alkyl halides,[10–12,26–29] deamination of aliphatic and alicyclic amines.[17,30–33] hydrocracking of paraffinic hydrocarbons,[34] hydrogenolysis of aliphatic aldehydes,[35] hydrogenation of aliphatic ketones,[36] deuterium exchange,[37] isomerisation of n-butenes,[38] adsorption and desorption of n-heptane in carrier gas–modified Al_2O_3 or porous glass systems,[39] and diffusion of ethylene, propene, and diethyl ether molecules in nitrogen.[40]

Together with the physicochemical applications, interesting possibilities of using SFGC for analytical purposes have been discovered (see below).

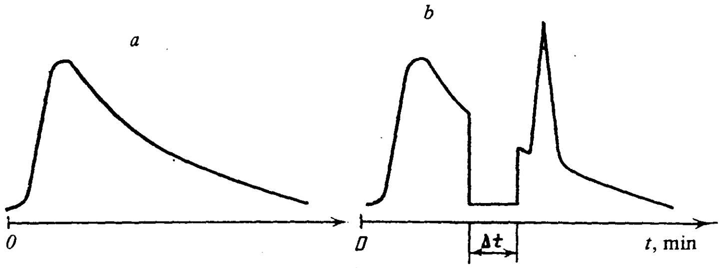


Figure 1. Approximate form of the chromatographic output curves for the reaction A → B in the column-reactor under the conditions of traditional eluent gas chromatography and gas chromatography with a single arrest of the carrier gas (for explanations, see text).

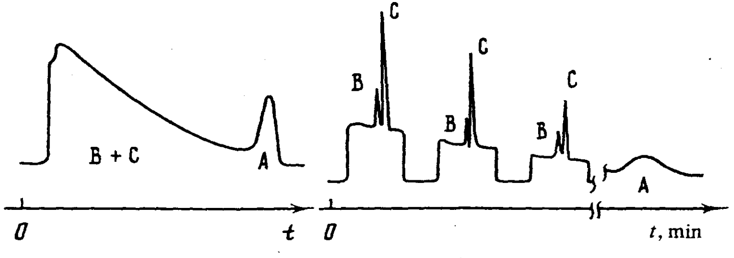


Figure 2. Chromatographic output curves for the reaction A → B + C in the column-reactor:[11] *a*) traditional eluent chromatography; *b*) SFGC.

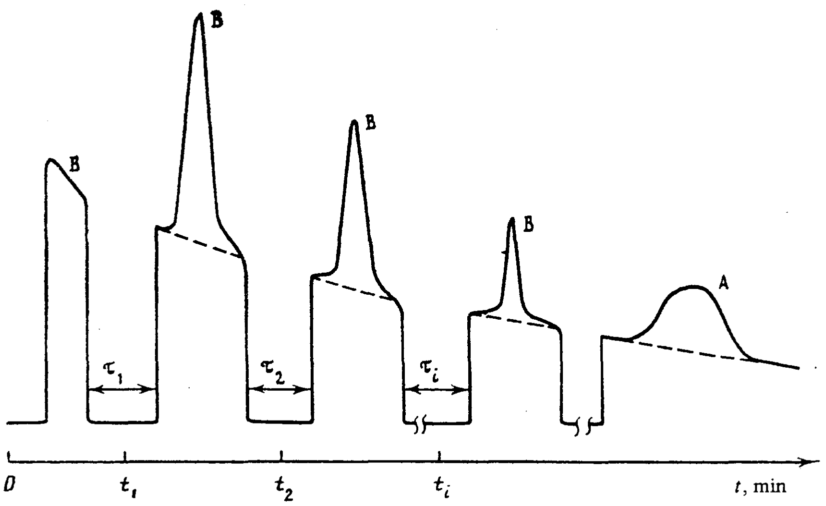


Figure 3. Typical chromatogram illustrating the possibilities of the SFGC method in the study of the kinetics of the first order chemical reaction A →B in the column-reactor (for explanation, see text).

2. Determination of the Rate Constants for Chemical and Physical First Order Processes

Phillips et al.[10] examined the possibility of investigating the kinetics of four types of first order chemical reactions by the SFGC method.

1. Isomerisation of A to B:

$$A \xrightarrow{k} B. \tag{2}$$

2. Decomposition of A with formation of one (B) or several products:

$$A \xrightarrow{k} B + C + \ldots \tag{3}$$

3. The formation from A of two (for example, B and C) or more products via independent parallel pathways:

$$A - \begin{cases} \xrightarrow{k_B} B \\ \xrightarrow{k_C} C \end{cases} \tag{4}$$

4. Consecutive conversion of A into B and then of B into C:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{5}$$

The initial approach to the interpretation of the experimental results[10–12] was based on the model of linear and ideal chromatography, which was itself based on two important assumptions: the constancy of the partition coefficients of the compounds eluted in the course of the experiment and the instantaneous establishment of equilibrium between the phases in the column-reactor. It was also assumed that the surface of the adsorbent-catalyst contains centres with identical catalytic activities and that, when the carrier gas flow is interrupted, the chemical reaction proceeds under rigorously static conditions. In this case, when the flow of the carrier gas is restarted, one records the so called "stop-peak", whose area is rigorously proportional to the amount of product formed during the arrest.

It has been suggested that the rate constant for the reversible first order reaction (2) be found from the equation

$$k = [\ln(P_1\tau_i/P_i\tau_1)]/f(t_i - t_1) \tag{6}$$

where P_1 and P_i are quantitative parameters (the areas or heights) of the first and *i*th "stop-peaks" respectively, τ_1 and τ_i are the durations of the first and *i*th arrests respectively, t_1 and t_i are the instants corresponding to the centres of the first and *i*th arrests respectively, and f is the fraction of reactant molecules sorbed by the active centres on the surface.#

If the product $kf\tau$ is fairly large (exceeds 0.3, which is rarely observed in the experiment), the rate constant is found from the equation

$$k = \{\ln[P_1 \sinh)(kf\tau_i)]/P_i \sinh(kf\tau_1)]\}/f(t_i - t_1). \tag{7}$$

In order to increase the accuracy of the calculation, it has been recommended[10] that the areas (or heights) of the most remote "stop-peaks", referring to the beginning and end of the reaction (Fig.3), be compared and that the calculation from the intermediate parameters (for close values of T) be carried out only in order to estimate the stability of the operation of the column-reactor and to find the order of the reaction.

#The numerical values of f are determined by the ratio $[t'_{RA}/t_M) - 1]t_M/t'_{RA}$, where t'_{RA} is the corrected retention time of the reactant and t_M the dead time. In the majority of cases f is close to unity (0.985–0.987). When the direct experimental measurement of t'_{RA} is impossible, it can be found indirectly.[29]

We emphasise that, in the derivation of Eqns.(6) and (7), the duration of the arrest of the carrier gas is not stipulated[10] and that in principle it can vary (shorter at the beginning of the experiment and longer at the end). The only important factor is that the time during which the carrier gas flow is stopped should be significantly shorter than the half-life of the reactant. However, if one specifies the constancy of the duration of the arrests, then the numerical value of k can be found graphically with the aid of the relation:[29]

$$\lg P = \mathrm{const} - \frac{kf}{2.303}\cdot t \quad . \tag{8}$$

In order to calculate k for reaction (3) by Eqns.(6) and (7), the areas or heights of the "stop-peak" for any one, two, or all the compounds formed are measured. The last method is preferable if the chromatographic bands of the products are sufficiently separated.

For parallel reactions, for example, reaction (4), the ratio of the quantitative parameters of the peaks of compounds B and C after each arrest of the gas flow should be constant and the observed rate constant for the consumption of the reactant ($k_1 + k_2$) is calculated, as in the previous case, from the sum of the areas or heights of the "stop-peaks" B and C. The ratio of the areas of peaks B and C, adjusted to the same detection sensitivity and recorded after each arrest of the carrier gas, is equal to the ratio of the rate constants k_B/k_C.

Finally, when the consecutive reactions (5) take place, the ratio of the quantitative parameters of the "stop-peaks" of the products B and C does not remain constant. Furthermore, only the "stop-peaks" B will be symmetrical on the chromatograph. The superposition of the "tails" of the peak due to the reactant A and of the band of the intermediate compound B (formed continuously from A) hinders the differentiation of the band of the product C, which is formed during the arrest of the carrier gas flow (i.e. the "stop-peak" C). As a result, the accuracy of the determination of the rate constants for both the first stage (from the sum of the areas or heights of the "stop-peaks" of compounds B and C) and for the second stage (from the areas or heights of the "stop-peaks" C) is reduced. The accuracy of the determination of k_2 can be increased by measuring the rate constants for the second stage in independent experiments when the pure substance B is injected into the column-reactor.

In 1975–1978 Katsanos and co-workers developed a theory of the SFGC method on the basis of more complex models taking into account the non-ideality and non-equilibrium nature of slow diffusion and sorption processes in the column-reactor[13,14] and discussed the characteristic features of a first order chemical reaction in a dynamic regime under the conditions of ideal chromatography[15] taking into account the experimentally established fact that several (at least two) types of active centres exist on the surfaces of aluminosilicate catalysts.[41]

In the discussion of their model, the authors[13–15] rule out the spreading of the "plug" of the reactant or adsorbate vapour localised in the initial section of the space within the column-reactor and make the assumption that the isotherm of the distribution of the adsorbed species on all the centres is linear and that there is no longitudinal diffusion in the gas phase. For non-reaction systems, it is assumed that the establishment of interphase equilibrium in the column-reactor is inhibited solely by adsorption–desorption processes.[13,14] On the other hand, in describing the behaviour of the reaction system, the influence of sorption and diffusion processes is ruled out and the instantaneous distribution of reactants and products between the stationary and mobile phases is postulated.[15]

Having analysed the material balance established in the column-reactor throughout three artificially specified time intervals—before the first arrest, during the arrest, and after the flow has been restarted, Katsanos obtained a fairly cumbersome expression relating the area or height h of the "stop-peak", the duration of the arrest of the carrier gas flow t_S, and the rate of formation of the products R:[30–33]

$$R = \alpha\frac{h}{t_s} = \alpha m\left\{\sum_{i=1}^{n}\frac{k_2^{(i)}k_1^{(i)}g^{(i)}}{\bar{k}_1 - k_2^{(i)}}\cdot\exp[-k_2^{(i)}t] - \left[\sum_{i=1}^{n}\frac{k_2^{(i)}k_1^{(i)}g^{(i)}}{\bar{k}_1 - k_2^{(i)}}\right]\cdot\exp(-\bar{k}_1 t)\right\} \quad , \tag{9}$$

where α is a proportionality constant, m the mass of the injected reactant, and $g^{(i)}$ the fraction of reactant A absorbed on the ith active centre:

$$g^{(i)} = k_A^{(i)}\Big/\left(1 + \sum_{i=1}^{n}k_A^{(i)}\right) \quad ,$$

k_1 being the sum of the products $k_1^{(i)}g^{(i)}$:

$$\bar{k}_1 = \sum_{i=1}^{n}k_1^{(i)}g^{(i)} \quad .$$

For the simplest case of the irreversible first order reaction A → D on active centres of only one type without the formation of the intermediate B–S, i.e.

$$\mathrm{A} + \mathrm{S} \rightleftarrows \mathrm{A{-}S} \xrightarrow{k} \mathrm{D{-}S} \rightleftarrows \mathrm{D} + \mathrm{S} \quad .$$

Eqn.(9) reduces to Eqns.(6) and (8). The applicability of Eqn.(9) has been confirmed in an experimental study by the SFGC method of the deamination of a number of aliphatic and alicyclic amines on the surface of Al_2O_3 [30,31] and silica gel[32] and also in a study of the kinetics of the dehydration of cyclopentanol and cyclohexanol on the surface of Al_2O_3 irradiated with neutrons in a nuclear reactor.[25]

In analysing the Katsanos model,[15] it is logical to assume that only part of the reactant is consumed in the formation of volatile products on the ith active centres of the adsorbent-catalyst; an appreciable fraction of the reactant can be sorbed irreversibly on active centres of another type with formation of involatile compounds, which should be manifested by a reduced conversion Q of the initial alkyl halide, alcohol, or amine. For example, in relation to the deamination of cyclohexylamine on two types of active centres on the Al_2O_3 surface, the following inequality holds for Q:

$$Q = (k_1^{(1)}g^{(1)} + k_1^{(2)}g^{(2)})\Big/\sum_{i=1}^{n}k_1^{(i)}g^{(i)} < 1 \, . \tag{10}$$

The similarity of the numerical degrees of conversion of the initial cyclohexylamine into cyclohexene, calculated by Eqn.(10) and found by means of independent direct measurement, which has been discovered by Vattis et al.,[33] characterises the Katsanos model as fairly flexible. Nevertheless, we emphasise that the elimination of the influence of sorption and diffusion processes on the establishment of interphase equilibrium in the column-reactor during a chemical reaction, which has been adopted in this model,[15] is an artificial procedure which facilitates a formal description of the system within the limits of the conditions formulated. In fact the rate of accumulation of the product in the gas phase is an additive quantity determined by the set of the stages involving chemical reaction in the condensed phase and partition in the condensed phase–gas system. Only when condition (1) holds, is it possible to obtain information about the chemical process from the results of headspace analysis. If, on the other hand, $k_r \gg k_e$, then the slope of the resulting relation will characterise the rate of mass exchange (the rate of extraction).

Under real experimental conditions, particularly in the study by the SFGC method of chemical reactions in solution in the stationary phase, situations frequently arise where $k_r \cong k_e$. The linear relation (8) is then transformed into a non-linear relation, because two exponential functions are superimposed, which is formally analogous to the case of two consecutive-parallel first order processes.

Thus the optimisation of the conditions under which headspace analysis is employed, including the conditions in a version of the SFGC method, for the investigation of the kinetics of the chemical process in the condensed phase should consist in seeking a regime ensuring the validity of inequality (1). In many instances, this problem can be readily solved when chemical reactions are carried out at fairly high temperatures on the surface of adsorbent-catalysts such as Al_2O_3, molecular sieves, and coarsely porous glass. At high temperatures, conditions governing the desorption of the volatile products formed do not limit the rate of their accumulation in the gas phase and the experimental relation (8) obtained makes it possible to find the constant for the rate of the chemical process on the surface of the adsorbent-catalyst.

3. Apparatus

The possibility of constructing gas connector schemes for SFGC on the basis of the experience gained in the development of combined gas-chromatographic analytical methods (interrupted gas chromatography) has already been mentioned above. The simplest versions of these schemes have been designed for use in a column-reactor linked directly to the detector (as a rule a flame-ionisation detector). The taps switching the gas flow are located outside the thermostatted zone directly ahead of the chromatograph evaporator.[10] In order to smooth the pressure drops in the system when the gas flow is switched off and then switched on, Katsanos and co-workers[13,29] used two consecutive stopcocks separated by a buffer reservoir (0.5–1.0 litre). We may note that this complication of the gas circuit of the apparatus is not essential, since the change in pressure in the column during the alternation of the arrest and flow of the gas has itself little influence both on the effectiveness and degree of separation. Thus, according to Walker and Wolf's data,[22] three consecutive arrests of the carrier gas flow lasting 0.5 min each caused a change in the effectiveness of the operation of the column and in the degree of separation of model hydrocarbon mixtures just as insignificant as a single arrest lasting 1.5 min.

The duration of the arrest of the carrier gas flow has a much greater influence on the spreading of the band in the column working in the SFGC regime. By carrying out comparative tests of three versions of the gas circuit, the authors[22] established that, when any one of the versions with both packed and capillary columns is used, brief interruption of the carrier gas flow (for 1–2 min) causes an insignificant alteration in the effectiveness and the degree of separation, which are, however, significantly reduced when the duration of the arrest is increased to several minutes. an analogous conclusion concerning the inverse proportionality between the duration of the arrest and the effectiveness of the column was reached in another study.[23]

A gas circuit similar to those employed in the studies mentioned[20,22,23,33] exhibits an appreciable inertia. Thus, according to data of Liebman et al.,[20] the lag during the period from the instant of turning the tap to the complete arrest of the carrier gas was 20 s, while according to other data[33] the difference between the specified and actual durations of the arrest reached 40 s. In the vast majority of studies carried out using SFGC, arrests of the carrier gas of identical duration (1–10 min) were specified and for this reason the corrections to the results of experiments associated with the inertia of the gas circuits were not made.

However, changes in the duration of the arrests of the carrier gas flow constitute a useful procedure when secondary processes accompanying the chemical reactions investigated appear, for example, autocatalysis by the water evolved or polymerisation of the olefins formed on dehydration of alcohols.[24] In those cases where the reactant arrest time is short, it is possible to formulate a series of experiments with single arrests of the carrier gas flow, which, however, are of different duration.[34,42,43] It has been observed[44] that, when very short arrests of the carrier gas flow are specified (down to 30 s, 5 s, or even 1.5 s), each resumption of the gas flow is accompanied by the recording of a negative signal.

In the majority of the reaction systems investigated by the SFGC methods, the expected composition of the product formed was fairly simple and there were no difficulties with their identification. In doubtful cases the procedure involving the trapping of the eluate fraction at the outlet from the column-reactor with its subsequent chromatography on analytical higher performance columns under the conditions of traditional eluent chromatography was resorted to. With the outlet from the reactor column connected directly to the detector, it is possible to obtain kinetic data for the variation of the overall composition of the products. The combined schemes, tested successfully in our laboratory,[45,46] are useful for the investigation of the kinetics of the formation of individual compounds. They include a column-reactor and an anlytical column located in autonomous thermostats of gas chromatographs (for example, of the Tsvet-100 series).

4. The Principal Results of Kinetic Studies by the SFGC Method

There exists a possibility, in principle, of using SFGC for the investigation of both heterogeneous catalytic processes and homogeneous reactions carried out in solution in the stationary and liquid phase (see, for example, Refs.11, 12, and 47). However, in practice the gas-adsorption version of chromatography is usually employed. Column-reactors 3–4 mm in diameter and 30–150 cm long are filled with adsorbents (Al_2O_3, modified alkali metal halides, silica gel, or coarsely porous glass) ensuring the stable retention of the reactant (alcohols, alkyl halides, amines, carbonyl compounds) and the rapid elution of the products of the dehydration, dehydrohalogenation, deamination, and hydrocracking reactions.

Experimental conditions under which the retention time of the reactant amounted to tens of minutes, hours, or even days while the retention time of the product was 1–5 min were selected for each type of reaction system, which made it possible to record tens and sometimes even hundreds of "stop-peaks" in a single analytical cycle for the duration of arrests of the carrier gas flow between 30 and 120 s.[11,24] The treatment of the experimental data consisted in the plotting of kinetic curves corresponding to an equation of type (8). Among the systems investigated, the simplest

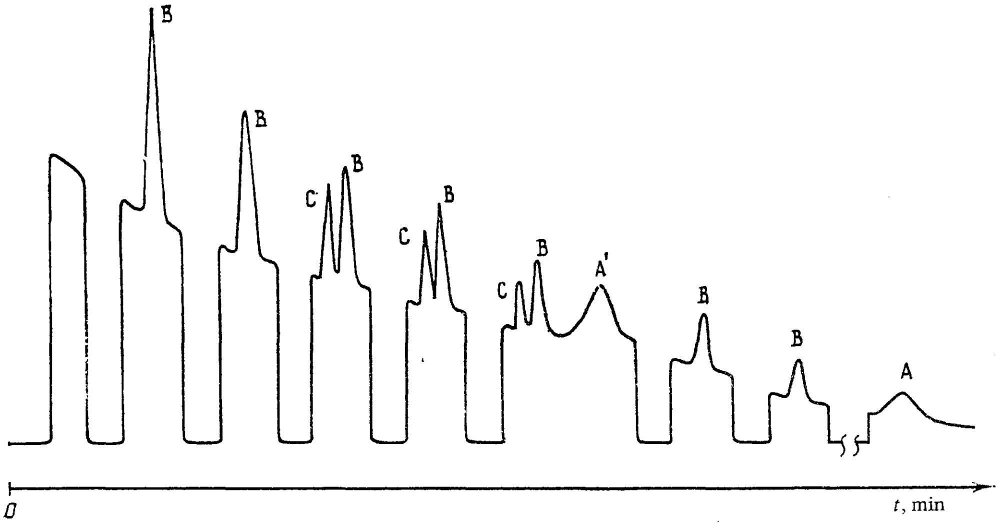
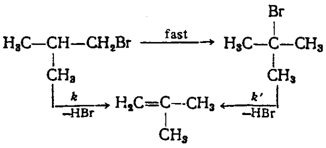


Figure 4. Chromatogram obtained in the study by the SFGC method of the dehydrobromination of isobutyl bromide on the surface of Al_2O_3 with 10 wt.% of LiCl:[27] A) isobutyl bromide; A') t-butyl bromide; B) isobutene (from isobutyl bromide); C) isobutene (from t-butyl bromide).

relations have been found for the dehydrohalogenation reaction. The reactants employed were cyclohexyl bromide, cyclohexyl chloride, cyclopentyl bromide[10] and also n-, s-, iso-, and t-butyl bromides.[33,34] The catalyst was γ-Al_2O_3 modified (10 wt.%) by the salts KCl, NaCl, CsCl, LiCl, KBr, NaBr, KI, and NaI. The reaction was carried out at different temperatures in the range from 50 °C to 150 °C. Depending on the specific reaction system and the experimental temperature, the numerical values of k varied from 20–30 s^{-1} to 30 min^{-1} and those of E_a from 50 to 130 kJ mol^{-1}. The simplicity and clarity of the experiment made it possible to recommend the investigation of the kinetics of the dehydrohalogenation of isobutyl bromide on an Al_2O_3 surface (with 10 wt.% of NaBr) by the SFGC method as a laboratory task in a University practical physical chemistry course.[29]§

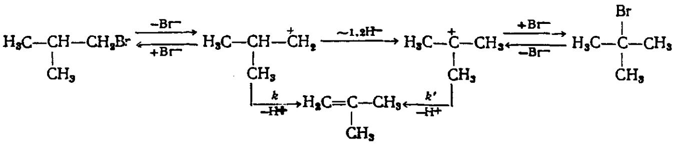
It has been possible to establish by the SFGC method[27] that the nature of the anion of the salt modifying agent has a major influence on the kinetics and mechanism of dehydrohalogenation. In particular, in experiments with isobutyl bromide and Al_2O_3, modified by alkali metal chlorides, after several single "stop-peaks" of the expected product (isobutene), two peaks began to be recorded on the chromatogram after each arrest of the carrier gas flow (Fig.4). The study of the kinetics for each series of "stop-peaks" showed that two parallel reactions take place in the column-reactor, one of which is described by a first order kinetic equation and the other by a zero or first order equation, but with a very low rate constant. On the basis of the evidence that both peaks observed are due to isobutene, the authors[27] suggested that the initial isobutyl bromide undergoes on the surface of the catalyst, together with the elimination of HBr, isomerisation to t-butyl bromide which subsequently also loses HBr with formation of isobutene:



The double "stop-peaks" continued to be recorded until the elution from the column of the broad band due to t-butyl bromide, after which (until the initial isobutyl bromide emerged from the column) single "stop-peaks" were recorded on the chromatogram as at the beginning of the experiment.

When Al_2O_3 modified by potassium iodide (10 wt.%) was used, double "stop-peaks" were also observed,[28] but, in contrast to experiments with Al_2O_3 treated with an alkali metal chloride, these continued to be recorded even after the initial reactant had emerged from the column. Hence it was concluded that in the given case the initial isobutyl bromide is converted, via the intermediate formation of carbenium ions, into an alcohol which is dehydrated very slowly at the selected temperatures (~80–100 °C) and which is very strongly retained by the active centres of the adsorbent.

However, if the multistage mechanism of the dehydrohalogenation of isobutyl bromide by Al_2O_3 modified using metal chlorides is represented by



taking into account the scheme examined by Katsanos and co-workers,[27,28] the problem arises how rigorous is the attribution of the markedly different numerical values of k and k' to the different reactivities of isobutyl and t-butyl

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§ A similar task has been successfully carried out for several years by the students of Course IV in the Gas Chromatographic Laboratory of the Faculty of Chemistry at Leningrad University.

bromides respectively. It is most probably caused by the differences between the stabilities and reactivities of the intermediate isobutyl and t-butyl cations.

We may note that the dehydrohalogenation reaction on the surfaces of the catalysts specified above are the only ones, among those investigated by the SFGC method, for which the carbenium ion mechanism has been adopted. For the related heterophase dehydration and deamination reactions, a concerted mechanism of the processes (*trans*-elimination) has been reliably demonstrated.

Another important result of the application of the SFGC method to the study of the elimination reactions is the conclusion that each can be carried out simultaneously on several (two–three) types of active centres on aluminosilicate catalysts. Attention was first drawn to this fact by Phillips et al.[12] The experimental kinetic curves for the dehydration of primary, secondary, and tertiary C_2–C_8 alcohols[24] on the surface of γ-Al_2O_3 with 10% of KCl were very close to the kinetic curve for the simultaneous decomposition of two radioactive isotopes. The conclusion that there are two types of active centres on the catalyst surface, drawn from the finding, is supported by the available information[41] concerning the presence of two types of aluminium ions in γ-Al_2O_3 (in tetrahedral and octahedral coordination states). Phillips and co-workers[24] do not rule out the presence on the surface of unmodified γ-Al_2O_3 and also of catalytic centres of a third type distinguished by an increased activity and suggested that the role of the modifying agent employed (KCl) consists in passivating these centres.

Subsequently the hypothesis of the possibility of the simultaneous dehydration on all three types of active centres was confirmed experimentally[25] and similar relations were observed also in the study of the deamination reaction.[32]

The observation of identical kinetic relations for the deamination and dehydration reactions on the surfaces of aluminosilicate catalysts is noteworthy. The experimental kinetic curves for both processes using different Al_2O_3, porous glass, and silica gel specimens as catalysts at relatively low temperatures pass through a maximum and then fall steeply. An increase of temperature leads to the disappearance of the ascending section of the curve and to the approach of the remaining descending branch to the form of a simple exponential relation.

Mathematical analysis of the kinetic curves obtained showed that they can be adequately described by the following empirical equations:

$$R = a_1 \exp(-b_1 t) + a_2 \exp(-b_2 t) + a_3 \exp(-b_3 t) \,, \tag{11}$$

$$R = \sum_{i=1}^{3} [a_i \exp(-b_i t)] - a_4 \exp(-b_4 t) \,. \tag{12}$$

where R is the rate of formation of the product and a_i and b_i are positive constants which depend on the catalyst, the reaction investigated, and temperature. Eqn.(11) is valid for processes which proceed with participation of two types of active centres on the catalyst surface (deamination of amines on the Al_2O_3 surface[30,31]), while Eqn.(12) characterises reactions occurring on active centres of three types (deamination of amines on the surfaces of coarsely porous glass and silica gel,[32] dehydration of alcohols on the Al_2O_3 surface irradiated with neutrons[25]).

Both empirical equations, (11) and (12), agree fully with Eqn.(9) proposed previously.[15] The rate constants k_1, $k_2^{(1)}$, $k_2^{(2)}$, and $k_3^{(3)}$ were found from graphical relations of type (13) or using non-linear regression analysis with the aid of a computer.[25]

Since the absolute numerical values of k (like the absolute retention parameters in gas chromatography) are influenced by various experimental factors (the characteristic features of the preparation and conditioning of a particular column-reactor, its size, etc.), it was suggested as early as 1970[24] that the relative reactivities of the substrates be estimated by the method of competing reactions, injecting simultaneously into the column-reactor a mixture of two alcohols—the test alcohol and one selected as the standard. Unfortunately, this procedure was not developed in the subsequent practical employment of SFGC. Furthermore, the error in the measurement of the absolute values of k, obtained in experiments on different apparatus and columns, can reach 400%, while the reproducibility of the relative quantity k_1/k_2 is to within 10–15%.[24]

As a consequence of the very strong sorption of alcohols on the Al_2O_3 surface, the reactants hardly move in the column-reactor along the catalyst bed, which makes it possible to carry out a very large number (tens and hundreds) of measurements in each individual experiment in the study of dehydration kinetics by the SFGC method. Throughout such a long cycle, it is possible to carry out a stepwise variation of the temperature of the column-reactor and to obtain data necessary for the determination of the activation energy E_a without resorting to the additional injection of reactants. Phillips and co-workers[24] note correctly that the inadequate accuracy of the measurement of the numerical values of E_a (±1.5 kcal mol^{-1}) precludes any reliable conclusions about the character of the variation of E_a as a function of structure within the limits of an isotypical series (for example, in the series of normal primary or normal secondary alcohols), which, in their view, would have been possible if the error could be reduced to ±0.5 kcal mol^{-1}. Nevertheless, their results[24] reveal an appreciable difference between the activation energies for the dehydration of primary alcohols, on the one hand, and secondary and tertiary alcohols, on the other. One should note the proportional variation of the numerical values of E_a and $\ln A$ (the pre-exponential factor in the Arrhenius equation), which indicates the operation of the so-called compensation effect.

Most of the results obtained in the above study[24] refer to the kientics of the dehydration reaction on "slow" active centres of the modified Al_2O_3. Katsanos and co-workers[25,32] determined and compared the numerical values of E_a and $\ln A$ for each type of "slow" and "fast" active centres on the catalyst employed in the deamination and dehydration reactions. Having confirmed the operation of the compensation effect in all cases, they concluded that each type combines a group of centres characterised by the same values of $\ln A$ but different E_a.[25]

The application of the SFGC method to the study of the kinetics of the hydrocracking of hydrocarbons on the Ni–SiO_2 surface at temperatures in the range 160–220 °C established unusually high values of E_a (300–550 kJ mol^{-1}); the values of E_a depend so strongly on the structural features of the compounds of a particular homologous series (n-alkanes, isoalkanes, and cycloalkanes) that this can be used in group analysis.[34]

Subsequently the behaviour of aliphatic aldehydes[35] and ketones[36] on the Ni–SiO_2 surface at temperatures in the range 130–200 °C was investigated. It was established that, under the given conditions, the reactions involving the hydrogenolysis of aldehydes and the dehydrogenation of ketones respectively predominate. The hydrogenation of aldehydes and the hydrocracking of the resulting alkanes are concomitant processes whose role increases with increase of temperature. At a temperature of 300–350 °C, the only reaction products are methane and water, which agrees with the data obtained in our laboratory¶ using a nickel–aluminium catalyst prepared in accordance with the recommendations of Grumbuller et al.[48]

Scott et al.[35] suggest that the hydrogenolysis of aldehydes is limited by two kinetically independent consecutive stages: the RCH_2CHO molecules adsorbed initially on the surface are slowly cleaved to the alkane RCH_3, which is desorbed to the gas phase, and the CHO fragment, which remains in the adsorbed state and is in its turn slowly reduced to CH_4.

Ketones are hydrogenated in one stage and the similarity of the kinetics of the reduction of the intermediate HCO in the case of aldehydes and adsorbed molecules of the ketones RR'CO, established by Abdulah and Sulaiman,[36] is an important experimental fact.

5. Application of Discrete Gas Extraction in a Single Chromatographic System to the Solution of Analytical Problems

As already mentioned above, apart from the rigorously stoichiometric reaction in the chromatographic column-reactor in accordance with schemes (2)–(5), some of the reactant molecules can be sorbed irreversibly on the surface of the sorbent-catalyst with formation of involatile compounds and can also be converted into side products (mainly relatively involatile polymers); sometimes, and this is especially characteristic of reactions in solution in the stationary liquid phase, the "breakthrough" of the reactant through the reactor is observed. The knowledge of the amount (fraction) of the reactant which has reacted is important for the estimation of the degree of conversion via the relevant pathway.

In the quantitative reaction of the reactant via pathways (2)–(5), the determination of its initial content in samples analysed having a complex composition is an important task for analytical reaction gas chromatography. The method of determining the initial concentration of the reacting compound, based on the knowledge of the kinetic parameters of the reaction, was first proposed in a study[49] where a pulsed chromatographic method was used to measure the reaction rate constant k and the current concentration of the reactant c_i at time t_i, this being followed by the calculation of the initial concentration c_0 by the familiar equation

$$k=\frac{1}{t_i}\ln\frac{c_0}{c_i}\ .$$

The method was tested in relation to the interaction of butadiene with maleic anhydride. The chromatographic reactor was placed beyond the separating column. The time of contact between the reactants was determined by carrying out experiments at different carrier gas flow rates on the assumption that the contact time is inversely proportional to the gas flow rate. In order to determine c_i, a non-reacting compound (internal standard) was introduced into the initial specimen. The disadvantages of this method are the long time required, the necessity for several analytical cycles with the reactor disconnected or connected at different carrier gas flow rates, and the difficulties in the selection of a suitable standard compound.

A chromatokinetic method has been developed recently[46] for the determination of the initial content of the reactant, based on the discrete extraction of volatile products from the reaction zone of the chromatographic reactor by the carrier gas. The combination in a single analytical cycle of the stages involving the measurement of the reaction rate constant k and the determination of the amount of products m_i formed during a fixed period t_i must be regarded as advantages of this method. The constant k was measured by the SFGC method using Eqns.(6) and (8). The amount of products formed during a specified time was found by the method involving the absolute calibration of the chromatograph. The method was tested successfully in relation to the dehydration of cyclohexanol and also s- and t-butyl alcohols to the corresponding olefins in a chromatographic column-reactor on the surface of a diatomaceous carrier coated with a layer of phosphoric acid. The initial content of the alcohol m_0 was found from a rearranged first order kinetic equation:

$$m_0=m_i/(1-e^{-kt})\ . \qquad (13)$$

The relative error of the determination did not exceed 10% on average.

Equations analogous to Eqn.(13) can be used also to determine the content of the substance which has reacted in the quantitative headspace analysis of reaction systems in autonomous reactors outside the chromatograph.[50,51]

A discrete gas extraction procedure, analogous to the SFGC method in its experimental aspect, has been used[52,53] to investigate the dynamics of desorption and to determine the overall content of volatile impurities in polymeric materials. The finely dispersed polymeric material was placed in a glass insert in one of two parallel evaporators of the chromatograph connected to the analytical column via a T-junction. The carrier gas was passed periodically either through the empty evaporator or through the chamber with the specimen, all the volatile products evolved into the gas phase during the preceding period being directed to the column. Since the rate at which the volatile impurities are transferred from the solid polymer to the gas phase is proportional to their concentration and formally obeys a first order kinetic equation, the overall content of the volatile component can be found, according to Kolb and Pospisil,[52,53] from the results of only the first two extractions.

The problem of determining the overall content of the volatile impurities diffusing from polymeric materials has been solved in a more general form by Ioffe and co-workers, who suggested that the results of discrete gas extraction in open systems be subjected to a treatment involving the measurement and subsequent allowance for the so-called buffer coefficient B, which characterises the fraction of the non-extracted substance and is equal to the ratio of the areas S or the heights h of the peaks on the chromatograms of the vapour phase obtained in two successive extractions:[54]

$$B=\frac{m_{n+1}}{m_n}=\frac{c_{G(n+1)}}{c_{G(n)}}=\frac{S_{n+1}}{S_n}=\frac{h_{n+1}}{h_n}\ , \qquad (14)$$

where m is the mass of the extracted substance, c_G the concentration of the extracted substance in the gas phase, and n the number of the extraction.

In the general case, the quantity B can change during extraction, but for analytical purposes systems characterised by constant buffer coefficients are the most suitable. For B = const, the amounts of substance contained in the extract form a geometrical progression with B as the denominator and the total amount of substance extracted M_0 can therefore be determined without carrying out an exhaustive extraction:

$$M_0=\sum_{n=1}^{\infty}m_n=\frac{m_1}{1-B} \qquad (15)$$

The number of successive extractions necessary for the accurate estimation of the buffer coefficient by Eqn.(14) should be as small as possible owing to the risk of the distorting influence of the "memory" of the apparatus and the

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¶ See B.V.Stolyarov and E.E.Galev "Tezisy Dokladov IX Vsesoyuznoi Konferentsii po Gazovoi Khromatografii" (Abstracts of Reports at the IXth All-Union Conference on Gas Chromatography), Kuibyshev, 1987 (in the press).

impairment of the phase equilibration conditions after many repetitions of the cycles involving flushing of the chamber with the specimen by the extractant gas.[55]

The authors of all the published studies on the practical employment of SFGC methods have failed to note the interfering influence of the above factors, although, according to the data of Ioffe et al.,[55] one cannot rule out the undesirable manifestation of the "memory" of the chromatographic system, especially after a large number of cycles involving the arrest and movement of the carrier gas. As a result of this, it is necessary to ensure fairly high concentrations of the compounds extracted in the gas phase and to confine oneself to the minimum necessary number of extractions for the solution of the given specific problem.

For a number of reaction systems resistant to high temperatures and characterised by low partition coefficients of the products formed, even a single arrest of the gas flow, sometimes combined with a sharp increase of the temperature of the column-reactor during the arrest, can ensure the quantitative conversion of A into B and the exhaustive extraction of the products from the condensed phase. The effective concentration of the impurities during their desorption from the surface of the sorbent in the absence of chemical reaction can be ensured in exactly the same way.[56]

The first example of the employment of the SFGC method for strictly analytical and not kinetic purposes has been the concentration, proposed by Phillips and co-workers,[11,12] of aliphatic alcohols as microimpurities from air or organic solvents on Al_2O_3 with their subsequent dehydration involving a single arrest of the flow (for 7 min) and with the simultaneous increase of temperature from 150° to 450 °C. The subsequent cooling of the column-reactor to the initial temperature and the restart of the carrier gas flow lead to the recording on the chromatogram of distinct olefin peaks, which are readily susceptible to integration.

A second example of the successful employment of a single arrest of the gas flow for analytical purposes is provided by a study carried out recently in our laboratory.† It was shown that a single arrest of the gas flow lasting 1 min is sufficient for the exhaustive hydrogenolysis of organic compounds of different classes on the surface of a nickel-aluminium catalyst in a hydrogen atomsphere at 350–400 °C. The new simple method for the determination of the total organic carbon in water and in aqueous solutions, developed in the above study, is based on the exhaustive conversion of carbon-containing compounds into methane, which is extracted in a single step by the mobile phase (hydrogen) from the surface of the catalyst. The relative error did not exceed 10% and the threshold sensitivity was 5 mg C $litre^{-1}$.

The disadvantages and limitations of headspace analysis in the SFGC version in the solution of both kinetic and analytical problems should be noted. In the first place, the method is applicable only to the investigation of processes whose kinetics are described by first order equations. The second disadvantage is the reduction of the accuracy of the measurement under the influence of diffusion of the extracted substance in the mobile phase during the arrest of its movement, which is aggrevated by the inertia of the gas circuit usually employed. An important limitation of the application of the SFGC method to the study of reaction systems is the necessity to ensure a greater retention of the reactant by the stationary phase compared with the retention of the products.

III. REVERSED FLOW GAS CHROMATOGRAPH

1. Principles, Apparatus, and Applications of RFGC

The gas chromatographic method with periodic change (reversal) of the carrier gas glow (RFGC), which is related to the SFGC method but is free from its main limitations, was proposed in 1980 by Katsanos.[57,58] The initial versions of the RFGC method were designed for the measurement of the kinetic parameters of chemical reactions on the surface of the adsorbent-catalyst in chromatographic column-reactors (a simple single stage first order reaction processes including two consecutive stages).[57,58] However, subsequently the applications of the method were greatly extended and RFGC was used to investigate the dynamics of adsorption and desorption, to measure the diffusion coefficients of volatile compounds in different gases, and to determine the activity coefficients of components of solutions.[59] The relative molar responses of the thermal conductivity detector and hence the molecular diameters and the critical volumes of different gases, the Lennard-Jones parameters, and the coefficients of the mass transfer of n-alkanes from the surface of Porapak P to a mobile gas phase (see below) have been measured recently by the RFGC method.

The fundamental possibilities of the RFGC method are illustrated in Fig.5. In contrast to SFGC, in the RFGC method the products concentrated in a limited volume of the mobile phase are sampled at fixed times by the repeated alteration of the direction of flow of the mobile phase and not by means of periodic arrests of the carrier gas flow. We shall consider one of the possible versions of the apparatus for the method. The reactor has the form of a T-piece, two arms of which (l and l') are alternately flushed with the carrier gas in opposite directions (F and R) by rotating the shell of the switching six-way tap ST (Figs.5*a* and 5*b*). The third arm L is at right angles to the first two and is used either for the evaporation of the reactant or for its pulsed injection directly into the adsorbent or catalyst bed. The catalyst or adsorbent are placed in sections l and l' in the stream of carrier gas. The gas circuit includes also the separating analytical column AC, which can be replaced by a permanent constriction. If after the injection of the reactant the position of the shell of the switching tap ST is altered periodically (at time intervals exceeding the retention time t_{RB} of the products in sections l and l' respectively), then one obtains a series of the so called F and R peaks associated with the movement of the gas in the forward (F) and reverse (R) directions. Each reversal of the gas flow then leads to the effective compression and symmetrisation of the band of the product continuously extracted from the reaction zone by the moving gas (Fig.5*c*).

The effectiveness of the concentration of the product in the gas plug directed to the detector can be increased by employing double flow reversal, which is entirely analogous to the replacement of single gas extraction by two consecutive extractions using the same volume of extractant gas. Having reversed at time $t_1 > t_{RB}$ the initial direction of the gas flow (F) to give the opposite flow (R) and without waiting for the recording of the peak of the extracted substance on the chromatogram, the tap is turned again, after a time interval Δt (several seconds) shorter than the retention time of the product t_{RB} in the l and l' sections of the reactor, returning the flow to the direction F. After recording the peaks of the products, the cycle is repeated, keeping constant the selected flow reversal time interval Δt. The form of the resulting chromatogram is illustrated in Fig.5*d*. If it is necessary to increase the extraction time during a

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†See B.V.Stolyarov and E.E.Galev, "Khimiya i Tekhnologiya Vody" (The Chemistry and Technology of Water) (in the press).

single cycle, the number of passes of the carrier gas through the l and l' reactor sections in the forward and reverse directions can be increased an even number of times.

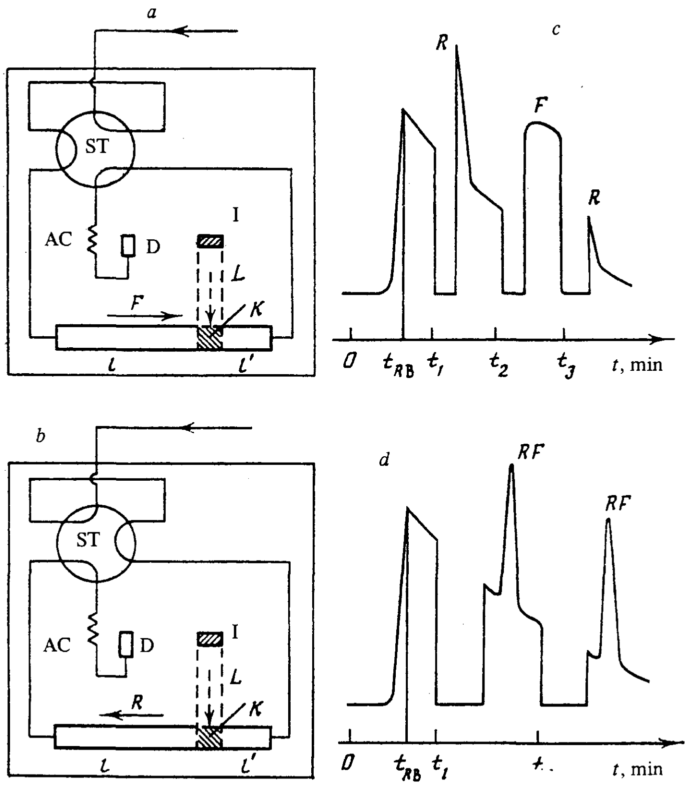

Figure 5. Schematic illustration of the apparatus for RFGC and specimen chromatograms (for explanation, see text).

For reaction systems with small and similar partition coefficients of the reactants and products between stationary and mobile phases and also in those cases where two gaseous reactants are used, none of which is the carrier gas, the catalyst bed is placed in the reactor branch L through which the carrier gas is not passed. The reactants (one or two) are introduced through the sample injection unit I; the end-face of the section is sometimes connected to a U-shaped tube containing 1–0.5 ml of the liquid reactant; a constant flow of the reactant vapour to the catalyst surface is thereby ensured.[59]

These procedures make it possible to investigate the kinetics of slow chemical reactions not only with respect to the reaction product but also with respect to the reactants provided that both are eluted from the catalyst bed together and are separated either in the sections l and l' of the reactor or in the analytical chromatographic column placed before the detector. In those cases where the volatile products and reactants pass from the reaction zone to the bulk of the carrier gas (i.e. to the reactor arms l and l') as a result of diffusional flow, this must be taken into account in interpreting the experimental results. The diffusion of the reactants and products in the carrier gas can be investigated in independent experiments using reactors unfilled with the sorbent.[60–63]

2. Determination of the Rate Constants for Chemical Reactions and Diffusion and Adsorption Coefficients

The analytical mathematical expressions permitting the determination of the equilibrium constant of a slow chemical or physical process from RFGC data depend on the process model adopted and on the chromatographic characteristics of the reactant and product.

We shall consider, for example, one of the simplest cases referring to first order reactions A → B, where the reactant A is rapidly adsorbed on the catalyst surface containing only isotypical active centres S. The compound A–S is then formed and is slowly converted into the adsorbed product B–S and the latter reaches equilibrium with the product B in the gas phase:

$$\mathrm{A}+\mathrm{B}\underset{K_\mathrm{A}}{\overset{\text{fast}}{\rightleftarrows}}\mathrm{A}-\mathrm{S}\xrightarrow{k}\mathrm{B}-\mathrm{S}\underset{K_\mathrm{B}}{\overset{\text{fast}}{\rightleftarrows}}\mathrm{B}+\mathrm{S}\ ,$$

where K_A and K_B are the partition coefficients of the reactant A and the product B respectively, with $K_A \gg 1$, and k is the reaction rate constant.

The kinetic experiment provides for the measurement of the amount of product accumulated in the gas phase volume of the reactor column during the time intervals between the successive changes in the direction of flow of the carrier gas, i.e. during the first R interval—from the instant t_1 (when the F direction changes to R) up to the instant t_2 (when the initial direction of the carrier gas flow is restored); the subsequent F interval extends from the instant t_2 to the corresponding instant t_3 when the direction of flow is switched (Fig.5c), etc. These time intervals should be shorter than the retention time of the reactant when the carrier gas moves in the forward and reverse directions.

Analysis of the material balance equation established for the system during the time intervals specified above makes it possible to relate the quantitative parameters of the F and R peaks (their areas or heights—P_F and P_R respectively) to the mass of the reactant m, the fraction of its molecules sorbed on the active surface centres f, the retention parameters of the product when it is eluted in the forward direction (t_R^F for the F peaks) or the reverse direction (t_R^R for the R peaks), and the total time (t_{tot}) elapsed from the instant of injection of the reactant to the subsequent reversal of the carrier gas flow:

$$P_R = mf\,[\exp(kt_R^F) - 1]\exp(-kt_{\text{tot}}); \qquad (16)$$

$$P_F = mf\,[\exp(kt_R^R) - 1]\exp(-kt_{\text{tot}}). \qquad (17)$$

In the case of a single stage first order chemical reaction of the type A → B under consideration, the graphical dependence of $\ln P_R$ and $\ln P_F$ on the time t_{tot} is represented by a straight line, from the slope of which the rate constant k can be found.

The physical significance of Eqns.(16) and (17) becomes more understandable when they are rewritten in the following form:

$$P_R = mf\exp[-k(t_{\text{общ}} - t_R^F)] - mf\cdot\exp(-kt_{\text{tot}}); \qquad (18)$$

$$P_F = mf\exp[-k(t_{\text{общ}} - t_R^R)] - mf\cdot\exp(-kt_{\text{tot}}). \qquad (19)$$

It is seen from Eqns.(18) and (19) that the peak areas are directly proportional to the retention times of the product with the carrier gas moving in the forward and reverse directions, so that all the experimental points should lie on a single straight line for rigorously identical lengths of the sections of the column-reactor ($l = l'$, Figs. 5*a* and 5*b*). When the lengths of the column-reactor sections are unequal, for example for $l' < l$, the *R* peaks should be smaller than the *F* peaks (and conversely). In this case the identical slopes of straight lines (18) and (19) can be regarded as proof of the absence of secondary effects (for example, the autocatalysis by the water evolved or the polymerisation of the olefins formed on dehydration of the alcohols) in the course of the conversion of the reactant A into the product B for different contact times with the active catalyst centres.

The non-linear character of the dependences of $\ln P_R$ and $\ln P_F$ on the time t_{tot} indicates a more complex process mechanism and the presence of not one but several rate-limiting stages. Some of them can be purely physical, for example, they can be determined by the slow diffusion of the reactant from the gas phase to the catalyst surface or the slow mass exchange of the products between the mobile and stationary phases.

In particular, in the study by the RFGC method of the deamination of aminocyclohexane on the γ-Al_2O_3 surface at 247 °C,[69] kinetic relations typical for two first order consecutive reactions were obtained. The application of RFGC to the study of processes with several consecutive-parallel first order stages has been examined by Katsanos and Kotinopoulos,[64] while Katsanos et al.[65] considered its application to the study of single stage reactions with a fractional order.

The case where the product and reactant are hardly sorbed on the catalyst surface and are eluted simultaneously is of special interest. This version has been considered in relation to the oxidation of CO to CO_2 by oxygen,[66] the hydrogenation of propene,[65] and the hydrodesulphurisation of thiophen to butane and butenes.[67] In solving problems of this kind, account must be taken of the complications associated with the diffusional flow of the reactant onto the catalyst surface. The concentration of the products or reactants at a fixed time is obtained by measuring the height of the corresponding chromatographic peaks. The concentration of the reactants depend on time, the diffusion coefficients, the catalyst mass, the volume flow rate of the carrier gas, and the rate of the chemical reaction. The concentration of the products depends in its turn on the rate of the chemical reaction, the mass of the catalyst, and the volume flow rate of the carrier gas. The expression for the reaction rate constant is as follows:[67]

$$k = \frac{v}{m_c}\ln\frac{1}{(1-x)},$$

where v is the volume flow rate of the carrier gas, m_c the mass of the catalyst, and x the fraction of the reactant converted into the product.

In particular, in the study of the reaction kinetics on the basis of the consumption of the reactant, we obtain the expression[67]

$$x = \frac{h_0^{(r)} - h^{(r)}}{h_0^{(r)}},$$

where $h_0^{(r)}$ is the height of the detector signal corresponding to the initial reactant concentration and $h^{(r)}$ the height of the detector signal corresponding to the concentration of the reactant which has passed through the catalyst bed.

3. The Principal Results of the Employment of the RFGC Method in Kinetic Studies

The reaction systems investigated by the RFGC method are of two types:

$$A \xrightarrow{\text{catalyst}} D + E + \ldots,$$

where A is the reactant strongly sorbed on the catalyst surface and undergoing slow decomposition and D and E are the volatile reactant decomposition products detected, and

$$A + Z \xrightarrow{\text{catalyst}} D + E + \ldots,$$

where A and Z are reactants weakly sorbed on the catalyst surface (one of them may be the carrier gas—for example, hydrogen) and D and E are the volatile reaction products detected.

The first group includes the dehydration of lower alcohols (propyl, isopropyl, and n-butyl[68]), the deamination of propyl-, isopropyl- and cyclohexyl-amines[68,69] on the surfaces of zeolite 13X and Al_2O_3, and also the catalytic cracking of cumene on the LaY and HY zeolites.[64] The second group combines the reactions involving the oxidation of CO by gaseous oxygen under the influence of Co_3O_4 deposited on Al_2O_3 modified with Ca^{2+},[66] the hydrogenation of propene on platinum (5% Pt on Al_2O_3),[65] and the hydrodesulphurisation of thiophen on the surfaces of catalysts with a complex composition, containing MoO_3 and Co_3O_4.[67]

The kinetics of the dehydration of alcohols have been investigated in the temperature range 179–385 °C, the first order of the reaction has been confirmed, and evidence for the absence of secondary processes on the catalyst surface has been presented.[68] The observed rate constants and activation energies agree fairly well with the literature data obtained by other methods, in particular by the SFGC method, using catalysts of similar composition.[24] Unfortunately, Katsanos and co-workers,[68] who previously employed actively the SFGC method for purposes including also the study of the kinetics of the dehydration of alcohols,[25] did not carry out direct experiments with the same reactants and catalysts for the purpose of the comparative assessment of the values of k and E_a obtained by the SFGC and RFGC methods. The only example of such a comparsion refers to the deamination reaction on Al_2O_3, the study of which by the SFGC and RFGC methods yielded results in satisfactory agreement.[33]

The reversal of the carrier gas flow made it possible to establish that the deamination reactions of propyl-, isopropyl-, and cyclohexyl-amines on the zeolite 13X in the temperature range 297–424 °C are described by a first order equation with a single rate-limiting stage, while on the active centres of γ-Al_2O_3 cyclohexylamine is deaminated via a mechanism including two consecutive first order reactions. With the aid of RFGC, it is possible to determine readily the numerical values of the rate constants for the rate-limiting stages, but the method does not enable one to discover to which particular stage each of the constants obtained refers.[69]

The most complex process investigated by the RFGC method is the cracking of cumene, catalysed by zeolites at 252 to 338 °C, to the study of the kinetics of which an extensive literature has been devoted.[64] It has been established that, depending on the nature of the catalyst, the kinetic process mechanism proposed previously[70] includes either one or two rate-limiting stages, but, as in the simpler cases considered before, the RFGC method does not enable one to find out which particular stages are rate-limiting.

It is noteworthy that compression of the product bands in the free volume of the reactor as a result of the reversal of the carrier gas flow leads to the loss of information about the number of types of active centres on the catalyst surface. In the interpretation of the RFGC data, this question is not even posed, while in studies on the theory[15] and the practical application[10,24,25,32] of the SFGC method much attention is devoted to precisely the determination of the role of the so-called "fast" and "slow" active centres of the catalyst.

On the other hand, the principle of the reversal of the carrier gas flow underlying RFGC made it possible to extend the application of the gas-chromatographic headspace analysis in kinetic studies and to include among such applications the study of reaction systems with reactants which are not retained on the adsorbent-catalyst bed, including systems with two gaseous reactants neither of which is the carrier gas. The study[66] of the kinetics of the oxidation of CO by molecular oxygen, catalysed by Co_3O_4 deposited on a zeolitic carrier modified with Ca^{2+}, is instructive in this respect.[66] The above study demonstrated experimentally the first order of the reaction with respect to CO, the reaction rate constants were determined in the temperature range 168–279 °C, and it was established that, with increase of the content of calcium ions in the catalyst (from ~0.4 to ~2.5 mmol g^{-1}), the activation energy for the oxidation of CO diminishes in proportion (from ~33 to ~14 kJ mol^{-1}) and then increases linearly (to ~44 kJ mol^{-1}). These observations clearly illustrate the possibilities in the employment of SFGC for the estimation of the comparative activities of catalysts of different composition.

The possibilities of the RFGC method are by no means restricted to the study of the kinetics of only first order processes. Thus a detailed investigation has been made[65] of the kinetics of the hydrogenation of propene by hydrogen and a catalyst comprising 5% of platinum on Al_2O_3 (carrier gas—nitrogen) at 136–166 °C. The fractional reaction order with respect to hydrogen, varying from 1.6 to 2.5 depending on the surface coverage of the catalyst by hydrogen, has been established by treating the experimental data using numerical methods.

Among the chemical reactions investigated by the RFGC method, the hydrodesulphurisation of thiophen to butane and butenes in a stream of hydrogen on aluminosilicate catalysts is of special interest.[67]

It is significant that the kinetic parameters of the diffusion and adsorption processes uncomplicated by accompanying chemical reactions can be investigated also in independent experiments using the RFGC method. Thus measurements have been made[60–62] of the diffusion coefficients in different carrier gases (H_2, He, N_2) for a series of lower gaseous alkanes and alkenes (both individual compounds and binary mixtures) and the temperature dependence of the diffusion coefficients has been found. A study has been devoted[63] to the application of the RFGC method to the measurement of the rate of evaporation of liquid C_5–C_8 n-alkanes and C_1–C_5 alcohols at 20–101 °C and to the simultaneous measurement of the diffusion coefficients of their vapours in helium. The adsorption of lower alkanes and alkenes on Al_2O_3 has been studied by Katsanos and co-workers,[71] while an investigation of the desorption of organic solvents (pentane, hexane, and acetone, and acetic acid) from the Al_2O_3 surface was described by the same workers in another communication.[72]

Slight changes in the experimental methods described above made it possible to determine, simultaneously with the measurement of the diffusion coefficients of air, oxygen, nitrogen, argon, CO_2 and lower gaseous alkanes and alkenes in the carrier gas (helium), also the relative molar sensitivities of the thermal conductivity detector with respect to the above substances and to characterise the critical volumes, molecular diameters,[73] and Lennar-Jones parameters.[74] The activity coefficients of methanol, ethanol, and 1-propanol in aqueous solutions at different concentrations have been measured by the SFGC method at 50°, 60°, and 65 °C respectively.[75] The application of RFGC to the determination of the mass transfer coefficients and also of the turbulent and longitudinal diffusion coefficients of hexane, heptane, and octane on columns filled with Porapak P (carrier gas—helium) has been discussed.[76]

We may note that the combination of the principles of RFGC and the circulation method proposed by Berezkin and Shiryaeva[77] may prove useful for the kinetic study of very rapid processes.

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The data described in this review permit the conclusion that stopped flow and reversed flow gas chromatographic methods possess great possibilities, which have not yet been ultimately elucidated, for the investigation of the kinetics of chemical reactions and slow physical processes (diffusion, evaporation, sorption) in chromatographic column-reactors and are also promising for the solution of certain important analytical problems (determination of volatile impurities and of the overall content of chemical elements in different objects, determination of the initial content of the reactant).

For the further development and effective use of the SFGC and RFGC methods, it is essential to optimise them using the mathematical experimental design procedures. However, one can already say that both methods considered constitute a convenient instrument in the rapidly developing gas-chromatographic headspace analysis of reaction systems.[46,50,51]

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Physical and Corrosion-electrochemical Properties of the Niobium–Hydrogen System

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Electrochemical and physical aspects of the dissolution of hydrogen in niobium with an ideal or a real structure are discussed. The interactions of hydrogen with various crystal lattice defects and the changes in physico-mechanical characteristics of niobium caused by hydrogenation are analysed. Data on the kinetics and mechanism of non-equilibrium cathodic and anodic processes on hydrogenated samples of monocrystalline or polycrystalline niobium are examined, and the changes in chemical stability towards corrosive media resulting from saturation with hydrogen are discussed.
The bibliography includes 122 references.

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I. INTRODUCTION

Niobium is one of the most corrosion-resistant metals. In recent years it has been used not only as an additive in the production of special alloy steels but also as a construction material. The rapid increase in the production and application of niobium has stimulated extensive studies of its corrosion-electrochemical properties in aggressive media, because the main areas of applications of this metal are in the chemical industry, in nuclear and hydrogen energetics, and in various new technologies such as microelectronics, apparatus construction, photoelectrochemistry, etc.

Niobium can readily occlude gases (H_2, N_2, O_2). Their absorption is accompanied by structural and phase changes in the metal. The gas most actively sorbed by niobium is hydrogen, and extensive studies of the effect of hydrogenation on the physico-mechanical characteristics and on the corrosion-electrochemical behaviour of niobium in corrosive media have recently been reported. The importance of this information is obvious, because the wide-ranging applications of niobium and its alloys have not so far been guided by an adequate understanding of the nature of the passive state of niobium and niobium alloys in hydrogenating media.

Published information on the corrosion-electrochemical behaviour of niobium containing dissolved hydrogen is scattered throughout a variety of papers reflecting the physical aspects of the problem, or discussing the corrosion resistance of niobium in aggressive media. Electrochemists and materials scientists are mainly interested in the time-scale of the chemical stability of niobium and its alloys in corrosive media under conditions in which the metal is hydrogenated and its passivity may be impaired.

Both theoreticians and experimenters are interested in the formation of various phases in the Nb–H system, depending on the amount of hydrogen absorbed, and the very large volume of hydrogen which can be sorbed (up to a concentration corresponding to the composition NbH_3) suggests potential applications of niobium not only in nuclear energy but also as an occluder in hydrogen generators. This review examines the thermodynamic properties of the Nb–H system, problems associated with the dilatation of the niobium lattice caused by the penetration and diffusion of hydrogen, and the interaction of hydrogen with various defects of the metal lattice, as well as the final result of this interaction: the change in the physico-mechanical characteristics of niobium.

II. THERMODYNAMIC CHARACTERISTICS OF THE NIOBIUM–HYDROGEN SYSTEM

Niobium at room temperature absorbs a negligibly small amount of hydrogen from the gas phase.[1] The dissolution process begins only when the surface has been activated by high-temperature heat treatment (in the case of saturation from the gas phase) or by cathodic polarisation (if an electrochemical method of saturation is used). In the latter case the solubility of hydrogen in niobium at 293 K is sufficient to give an atomic ratio $\Phi_{H/Nb}$ as high as 0.68, the amount of hydrogen absorbed depending on the purity of the niobium.[2] In niobium of 98.5% purity the solubility (P_M) is 10 400 cm^3 H_2 per 100 g of metal (M), whereas in 94.8% Nb P_M = 5500 cm^3 per 100 g M, i.e. it is lower by about a factor of 2.

Structural characteristics of niobium hydrides.

Phase	Arrangement of metal atoms	Arrangement and coordination of hydrogen atoms	Stoichiometry and structure type	System, space group	Parameters of unit cell, Å	z	Refs.
α (>440 K)	b.c.c.	Disordered, tetrahedral	—	Cubic, *Im*3*m*	$3.43<a<3.45$	2	[11,13]
ζ (212—232 K) *	b.c.r.	Ordered, tetrahedral	Nb_2H	Orthorhombic, *C*222	$a\approx b=4.9$; $c=3.47$	2	[14]
β *	f.c.r.	ditto	NbH	Orthorhombic, P_{nnn} or C_{ccm}	$a=4.85$; $b=4.92$; $c=3.47$ ($\Phi_{H/Nb}=1$)	4	[11,12, 15,16]
γ (<180 K)	b.c.c.	»	NbH	–	$a=3.44$	—	[11]
λ	–	Ordered	NbH ($\Phi_{H/Nb}\approx0.8$)	Cubic	—	—	[12]
ε	—	Ordered	Nb_4H_3	—	$a\approx b=9.8$; $c=3.47$	—	[15,17, 18]
δ	f.c.c.	Ordered, tetrahedral	NbH_2	Cubic, *Fm*3*m*	$a=4.55$	4	[19]

Symbols: b.c.c., body-centred cubic; b.c.r., body-centred rhombic; f.c.r., face-centred rhombic; f.c.c., face-centred cubic lattice; *z* is the number of atoms in the cell.

*For these phases the coordinates of the wave vector **k** are (½, ½, 0).

The early workers[3–5] could not detect hydride phases corresponding to a definite stoichiometric ratio in hydrogen-containing niobium. However, a detailed phase diagram of the Nb–H system has now been assembled (Fig.1) by the application of X-ray, neutron, and electron diffraction methods.[6,7] At room temperature an increase in the $\Phi_{H/Nb}$ ratio is accompanied by a gradual α → β transformation, followed by the formation of a (β + γ) phase. The phase diagram was constructed by using very pure niobium (99.99 at.%); the α and α′ phase are disordered solid solutions of hydrogen in a body-centred niobium cubic lattice, in which the hydrogen (5–6 at.%) in the α phase occupies tetrahedral positions. Increasing $\Phi_{H/Nb}$ results in the formation of a β phase which is an ordered interstitial solid solution of hydrogen in niobium. The α and β phases can coexist at 293 K up to $\Phi_{H/Nb}$ = 0.73.

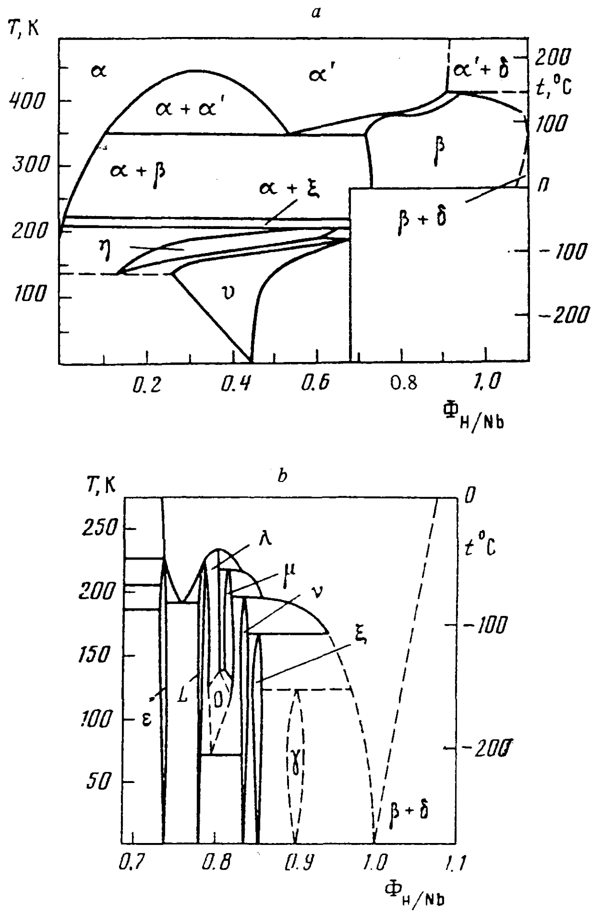


Figure 1. (*a*) Phase diagram of the Nb–H system; (*b*) low-temperature region of the phase diagram, for high concentrations of hydrogen in the niobium.[6,7,8–10] The broken lines define the regions for which no experimental data are available.

According to X-ray diffraction studies[11,12] the β phase has a face-centred rhombic lattice, and the α phase disappears at $\Phi_{H/Nb} > 0.73$. At $\Phi_{H/Nb} \leq 1.05$ only the β phase is observed (see Table), but at higher values of $\Phi_{H/Nb}$ a δ phase appears within the β phase, with a face-centred cubic lattice and corresponding to the compound NbH_2. The structural characteristics of the stoichiometric niobium hydrides are listed in the Table. Since a large proportion of the tetrahedral positions in the δ phase is occupied by hydrogen atoms, there is a high probability that the octahedral pores also may be occupied under suitable conditions, but so far we have no experimental proof of the existence of the compound NbH_3. However, we should not forget that the kinetics of the transformations in the H–M systems can be strongly affected by exposure to X-rays.[20]

Electron microscope studies, both morphological and in transmission, have shown that both the β phase in the α structure and the δ phase in the β matrix consists of long needle-like formations resembling the β phase in titanium and its alloys. Of course, phase transformations giving rise to precipitates having a volume greater than that of the matrix produce hydrogen "embrittlement" in the main structure, accompanied by rearrangements in the fine structure.

Various experimental methods can be used in the construction of phase diagrams, and the shape of the curves separating the existence regions of the phases depends on the chosen method. Details of various regions of the Nb–H diagrams have recently been determined, both at low ($\Phi_{H/Nb} \leqq 0.5$) and at high hydrogen contents ($\Phi_{H/Nb} = 1$). Thus, an unknown region of high hydrogen concentration between liquid helium temperatures and room temperature has recently been studied.[8] A combination of transmission electron microscopy and metallographic analysis has shown that a previously unreported[7] λ phase has an anisotropic cubic structure and can exist at $\Phi_{H/Nb} = 0.78$–0.81 and 207 K. At these very high hydrogen concentrations the precipitation of stoichiometric compounds of the Nb_4H_3 type (ε phase) is accompanied by the appearance of active H–H interactions and of lattice dilatation processes (discussed below). A detailed study of the phase diagram for $\Phi_{H/Nb} \leqq 0.5$ has shown[9] that the coexistence region of the α′ and the β phase is wider than suggested by X-ray measurements of lattice constant.[7] It has been reported[10] that regions of existence of η and θ phases can be identified at $\Phi_{H/Nb} < 0.7$ and temperatures below 200 K; the ν, *L*, *o*, μ, γ, and ξ phases also proposed have not yet been adequately investigated but will probably be confirmed by various experimental methods (as was done for the α, β, and δ phases).

As was stated above, Nb–H phase diagrams constructed from different experimental data can be markedly different. Thus, according to the Horner and Wagner theory,[21] which describes the H–H interaction as the result of the elastic anisotropic distortion of the lattice produced by the interstitial hydrogen atoms, the maximum in the curve separating the α′ and the (α + α′) phases is at 470 K and $\Phi_{H/Nb} = 0.36$, whereas according to measurements of lattice constants by X-ray diffraction this maximum lies at 443 K and $\Phi_{H/Nb} = 0.3$. These discrepancies probably arise because the samples (of different geometry) used in the various measurements contain a range of native structural defects, and the structure-sensitive methods used by different workers have different responses to the different types of defect produced by hydrogenation.

We should stress the need to allow for the geometric shape of the sample and for the extent of deformation in studies of phase transitions in the hydrogen–niobium system. Thus, a study[22] of the α–α′ transformation by X-ray structural analysis showed that in Nb–H alloys the lattice constant and the shape of the (440) line (from which the extent of the transformation was assessed) are strongly dependent on the extent of deformation and on the geometric shape of the sample (disk, foil, or wire). This effect should, of course, be correlated with differences in the concentration profiles in samples of different geometry.

Our understanding of phase transitions in the niobium lattice has been improved by studies of structures containing added hetero-atoms (O, N) by neutron-spectroscopy and resonance methods. The interaction of hydrogen with atoms of the matrix can be determined by both attractive and repulsive forces, depending on the type of deformation produced by the impurity atom. If the additive causes compression of the lattice the repulsion is predominant, but in the opposite case the predominant effect is attraction. The interaction of the hydrogen atoms with the lattice atoms is treated as the sum of contributions from electronic, elastic, and screening interactions with the ionic core of the lattice. For niobium (a typical 4d metal[23]) we can use the following empirical rule: impurity atoms from positions to the left of niobium in the Periodic Table act as hydrogen traps, whereas other atoms do not.

III. HYDROGEN IN THE IDEAL NIOBIUM LATTICE

It follows from the above discussion that hydrogen can exist in different states in the niobium lattice, and give phases corresponding to definite stoichiometric ratios, depending on the concentration of hydrogen absorbed by the metal. The hydrogen can be present both as dissolved atoms, occupying tetrahedral positions in the niobium lattice, and as H^- ions for high values of $\Phi_{H/Nb}$ (when niobium hydrides are formed).

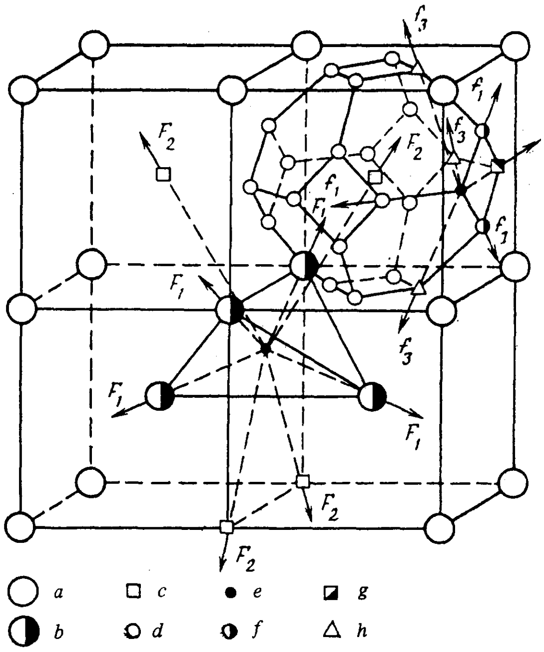


Figure 2. Radial Kanzaki forces (*F*) and H–H interaction forces (*f*) for stable positions of the hydrogen atoms in the tetrapores of the niobium lattice (the subscripts *1*–*3* denote the number of the coordination sphere).[28] In the diagram *a* are Nb atoms, *b* are Nb atoms of the first coordination sphere, *c* are Nb atoms of the second coordination sphere, *d* are tetrapores, *e* are H atoms, *f* are tetrapores of the first coordination sphere, *g* are tetrapores of the second coordination sphere, and *h* are tetrapores of the third coordination sphere.

Extensive experimental results obtained by neutron diffraction analysis and proton magnetic resonance methods show that tetrapores of three types (*x*, *y*, and *z* positions) are the stable sites for the introduction of hydrogen atoms. The radii of the hydrogen atom, of the tetrapores, and of the octapores are, respectively, $r_H = 0.0460$ nm, $r_T = 0.0426$ nm, and $r_0 = 0.0225$ nm. Hence $\Delta r = r_H - r_T \cong 0.003$ nm, and therefore the stabilisation of a hydrogen atom in an interstitial site should produce an anisotropic deformation of the lattice.[24,25] This results in the partial filling of the octapores, with an occupancy of the tetrapores of ~1/6.[26] The probability of hydrogen atoms with parallel spins being accommodated in adjacent interstitials of the first and the second coordination spheres is believed to be low. At high levels of hydrogenation ($\Phi_{H/Nb} \leqq 2$) the octahedral positions also can be partially filled with hydrogen atoms,[27] before the complete filling of the tetrapores.

According to Somenkov[26] when a tetrapore is filled with protium or deuterium (since the additional lattice distortion produced by the replacement of hydrogen by deuterium is small) the radial distribution of Kanzaki forces (the virtual forces acting on the neighbours of the inserted atom) takes the form shown in Fig.2. The Figure also shows the mutual disposition of the tetrapores in the Nb crystal lattice and the forces acting on the hydrogen atoms within these pores. A hydrogen atom of the centre of a tetrahedral pore produces an anisitropic deformation of the lattice. If another hydrogen atom is present in a neighbouring pore this deformation results in H–H interaction (or self-trapping), which is most marked under conditions of spin reorientation. If the hydrogen atom in adjacent interstitials have antiparallel spins the H–H interaction results in the formation of stable pairs. With a parallel arrangement of the spins the situation is less favourable to the formation of stable pairs. The stability of hydrogen in tetrapores has been experimentally demonstrated by neutron diffraction measurements.[26] The development of stable H–H interactions is accompanied by "swelling" of the hydrogenated crystal. Without allowing for anisotropic lattice deformation we can evaluate the relative change in volume $\Delta v/\Omega$ (where v is the volume of the unit cell and Ω is the atomic volume) per unit concentration of hydrogen, of deuterium, or of tritium (c) as $\Delta v/\Omega = 0.174 \pm 0.005$ for low c and $\Delta v/\Omega = 0.14 \pm 0.08$ for high c.

The filling of the d level by the 1s electrons of the hydrogen strengthens the M–M bond, and this should affect the mechanical characteristics of the niobium crystal in the hydrogenated state (plasticity, shock viscosity, strength, etc.). These characteristics are strongly dependent on the local dilatation of the Nb lattice, caused by the formation of hydride in limited volumes,[29] which stimulates the rearrangement of submicrostructures and thus affects the corrosion-electrochemical properties of niobium. The formation of clusters involving hydrogen is determined by the diffusional transport of the hydrogen in the lattice.

The diffusion problem can be discussed either in terms of the classical "jump" mechanism, according to which the diffusion act requires an amount of energy sufficient for a hydrogen atom in a tetrapore to surmount the diffusion barrier, or (in quantum-mechanical language) by identifying the interstitial atom with a small polaron, whose displacement is non-activated (tunnelling, or under-barrier transition).

According to Stoneham[30] there are two major differences between the quantum and the classical theory of diffusion of hydrogen in metals. The first is the quantisation of the energy levels, the second is the existence of a zero point relative to which the lattice distortions can be determined in the neighbourhood of a light impurity atom. In the jump mechanism for the displacement of hydrogen in the metal the probability of a jump is described by a simple equation of the Arrhenius type:

$$\Gamma \sim J^2 \cdot \exp\left(-E_a/k_B T\right) \tag{1}$$

where J is a tunnelling matrix element, given by

$$J = \frac{8\hbar^2}{2md^2}\left(\frac{2md^2}{h^2}\Delta\psi\right)^{3/4} \cdot \exp\left[-\frac{2}{\pi}\left(\frac{2md^2}{\hbar^2}\Delta\psi\right)^{1/2}\right] \tag{2}$$

and m is the number of the metal atom, d is the distance between the potential minima (the positions of the hydrogen atom in a stable state), and $\Delta\psi$ is the depth of the potential well.

Calculations[30] of the tunnelling matrix elements by formula (2) show that for niobium J is determined essentially by d and amounts to 1.45 MeV. The exponential factor in Eqn.(2) corresponds to a configuration in which the adjacent positions occupied by a proton before and after the diffusion act are equivalent.

The theory of small polarons treats a proton in a potential well before the diffusion act as having a lower energy than the adjacent interstitials. At the completion of the diffusion act the opposite situation exists. In the classical diffusion theory the quantity E_a corresponds to the relaxation energy at the instant when the proton is half-way to the second interstitial. Recent developments in the theory of small polarons have shown the need to allow for the dependence of J on the normal coordinates of the vectors for the displacement of the Nb atoms from their equilibrium positions. In this case, since in a b.c.c. metal lattice the hydrogen atoms are accommodated in tetrahedral interstitials, according to Flinn and Stoneham[30] the parameter Γ also depends on E_s (the energy needed to create a lattice configuration with normal coordinates large enough to give $J = J_{\lim} = \text{const}$):

$$\Gamma = \frac{J_{\lim}^2}{4\hbar\,(E_a E_s)^{1/2}} \cdot \exp\left[-(E_a + E_s)/k_B T\right] \tag{3}$$

Thus the localised proton moving through the lattice by a thermally activated process to a large extent "determines" the barrier which it must overcome. The diffusion problem is mor complicated when the adjacent interstitial is occupied by a proton or by some other light impurity element. In this case the H–H interaction results in a more substantial deformation of the neighbouring interstitial, and the diffusion process is facilitated for the pair of hydrogen atoms. Of course, in an ideal crystal the diffusional displacement of hydrogen is anisotropic and occurs preferentially along certain crystallographic directions. Surmounting saddle-points in the lattice must be discussed with allowance for the interaction between migrating particles even when the proton is identified with a small polaron. At low concentrations of hydrogen in niobium ($c_H \leqq 0.06$ at.%) the parameter E_a is linearly dependent on c_H. According to recent work,[31] and in contrast to earlier reports,[30] the average probability of a jump by a hydrogen atom in a niobium crystal for $c_H \leqq 0.06$ at.% is

$$\Gamma = \omega \cdot \exp\{-[(E^b - E^a)/4 + e_0]^2/e_0 k_B T - B^2/k_B T\}/B \tag{4}$$

where w is the vibration frequency of the hydrogen atom in the pore, and the quantities $(E^b - E^a)$, e_0, and B allow for the energy of the interaction between the diffusing hydrogen atoms.

It follows from (4) that the jump probability of a hydrogen atom in a niobium crystal, which depends on the activation energy for diffusion, is related to the vibration frequency of the hydrogen atoms in the pores, and therefore also to the mass of the hydrogen isotope. The strong dependence of the diffusion of hydrogen in metals on the mass of the isotope and on the type of crystal lattice was stressed in a recent interview.[32] It was pointed out that in a b.c.c. metal the diffusion parameter E_a is smaller for protium than for deuterium, whereas the opposite is true in metals with a f.c.c. lattice. The activation energy for the diffusion of protium in tantalum and in niobium suddently decreases at $T < 250$ K, but it remains constant for deuterium and tritium. This shows that the quantum effects are more substantial in b.c.c. than in f.c.c. metals. On lowering the temperature stronger effects are observed.

It was reported[28] that E_a for the diffusion of hydrogen isotopes in the b.c.c. niobium lattice at 133–373 K increases with the mass of the isotope, as also found by other workers.[32] However, it was also noted[28] that in the niobium samples the pre-exponential factor in the Arrhenius expression (1) is almost independent of the mass of the isotope. In that work[28] the diffusion process was discussed in terms of the Gorskii effect, for which the stress relaxation force Δ_E (allowing for the motion of the isotopes in a field of elastic stresses) is given by the Curie–Weiss expression

$$\Delta_E = A\frac{c_H P^2}{T - T_s} \quad , \tag{5}$$

where A is a constant depending on the elastic properties of the sample; T_S is the concentration-dependent spinodal temperature, which can be expressed as $T_S = uc_H/k_B$ for small concentrations of hydrogen in the metal (where u is the interaction energy); $3P$ is the dipole moment of the elastic deformation tensor (due to the presence of hydrogen), with $P_{ij} = \sum_m F_i^m x_i^m$ (F_i^m are the virtual Kanzaki forces acting on each atom m at a distance x_i^m from the defect site).

Therefore, as was stated above, it is essential to allow for the anisotropic dilatation of the lattice and for the change in lattice parameter a caused by the hydrogenation, which can be expressed as

$$\Delta a/a = (2c_H/a^3)P(S_{11} + 2S_{12}) \quad , \tag{6}$$

where S_{11} and S_{12} are the elastic coefficients.

An analysis of experimental data for the niobium–hydrogen system has shown[12] that $\Delta a/a$ can be found by assuming a linear dependence of a on the concentration c_H:

$$\Delta a/a = (4.72 \pm 0.25) \cdot 10^{-4}\, c_H \quad , \tag{7}$$

(where c_H is in at.%). By using (7), which is much simpler than (6) but does not allow for the anisotropic deformation of the lattice produced by hydrogenation, the concentration of hydrogen dissolved in the niobium can be determined with acceptable precision. From the results of various workers, reviewed in Ref.29, linear dependences of $\Delta a/a$ and $\Delta V/V$ (where V is the macroscopic volume of the sample) on the concentration of hydrogen in niobium are observed up to $\Phi_{H/Nb} = 1$. At attempt was made to explain these results in terms of the elastic interactions between hydrogen and niobium atoms by identifying the $\alpha \rightarrow \alpha'$ transition[33] with a gas → liquid transition.

It has also been reported[28] that at low concentrations of the hydrogen isotopes in niobium ($\Phi_{H/Nb} \cong 0.1$) the parameter E_a increases with the mass of the isotope (from hydrogen to tritium) from 0.068 to 0.133 eV, while the diffusion coefficient D_H is almost independent of the mass of the isotope.

IV. INTERACTION OF HYDROGEN WITH DEFECTS IN THE NIOBIUM CRYSTAL LATTICE

We have pointed out above the H–H pair interactions affect the diffusion of hydrogen. The hydrogen trapping phenomenon is found not only in interstitials but also in defects at higher dimensionality (vacancies and dislocations, single or in groups, grain boundaries, microscopic inclusions, and pores). The surface of the sample can also be treated as an energy trap. Let us examine the interaction of hydrogen and niobium with crystal lattice fectes of various dimensionalities.

1. Zero-dimensional Defects

The trapping of hydrogen by vacancies and vacancy clusters, by interstitial impurities (O, N), and by substitutional impurities (W, Mo, V, etc.) is of interest from the theoretical as well as from the practical standpoint. The latter impurities, being getter elements, have a substantial influence on the functional properties of Nb, especially those of technological importance (plasticity, shock viscosity, refractoriness, and corrosion resistance).

The hydrogen–vacancy interaction and the formation of vacancy–interstitial (hydrogen atom) pairs are usually treated as separate aspects in published papers. Hydrogen taken up by a single vacancy stabilises it and suffers a loss in diffusional mobility. However, it is possible for several hydrogen atoms to be adsorbed at a single vacancy, and this produces an anisotropic deformation of the lattice which results in an increase in the diffusional mobility of the vacancy–interstitial hydrogen atom pairs in some crystallographic directions. At high values of c_H the vacancy is transferred from one hydrogen atom to the next by a kind of "relay" mechanism.

Allowance for the change in mobility of the vacancy–interstitial hydrogen atom pair is essential at temperatures close to the melting point. "Anomalous superplasticity" has been observed experimentally in iron at high temperatures.[34] In the hydride-forming 4*d* metals, which include niobium, an increased concentration of hydrogen at the grain boundaries (i.e. at the sites where point defects are annihilated) may explain the change in mobility of these boundaries at relatively high temperatures. In materials previously deformed by large amounts (>90%) annealing after hydrogenation can yield larger-grained or even monocrystalline structures.

A study[35] of the low-temperature desorption of hydrogen from niobium has shown that at $T < 300$ K the formation of vacancy–hydrogen complexes is energetically favourable only for c_H values above the threshold of $\Phi_{H/Nb} > 2$. Further addition of hydrogen results in the merging of hydrogen–vacancy complexes into bubbles, detectable as low-temperature blistering (localised breakdown of the near-surface layer of metal).

Hydrogen can assist the combination of divacancies into vacancy clusters. The most stable clusters were found[31] to contain between three and six vacancies. Under these conditions we can expect the formation of gaseous hydrogen and pores of vacancies. However, because of the difficulty of producing vacnacies in b.c.c. metals very few experimental observations of this phenomenon have been reported, though one report[7] of the formation of screw dislocations near clusters of vacancies filled with hydrogen, detected by transmission electron microscopy, is noteworthy. The effects caused by the interaction of hydrogen in niobium with oxygen and nitrogen impurity atoms have been studied much more extensively.[37]

Nitrogen and oxygen atoms have relatively low mobilities in the niobium lattice at low temperatures, and therefore the capture of hydrogen atoms by nitrogen and oxygen atoms produces pairs with well defined configurations. Under conditions in which the interstitial oxygen atoms occupy octahedral positions the O–H pair can have a trigonal symmetry, i.e. be oriented in the <111> direction. The elastic interaction energy between an interstitial impurity accommodated in an octahedral position and a proton in an adjacent tetrapore has been calculated.[38] In this case the elastic energy is described by the expression

$$E = -F_0 Z F_T - \Delta E_s + \Delta E_0 \quad ,$$

where F_0 and F_T are the Kanzaki forces for interstial impurities in an octapore and a tetrapore respectively, Z is the harmonic lattice function in the near-surface layer of the pure metal, ΔE_S is the energy of the H–H bond, and ΔE_0 is the binding energy of the proton on the zeroth energy level.

Experimental studies,[39,40] mainly by elastic relaxation methods in the frequency range 30–170 MHz, have shown that the hydrogen atom can occupy tetrahedral positions when pairs with a <100> orientation are formed preferentially. This suggests that the hydrogen atoms are not localised in the tetrapores but are uniformly distributed in ring-like structures consisting of four tetrapores and four triangular sites (0, 3/8, 3/8) and surrounding an octapore not containing an oxygen atom. In this case the motion of hydrogen in the Nb lattice is accurately described by the Flinn–Stoneham theory [see Eqn.(3)]. It has been reported[32] that nitrogen atoms in niobium lower the diffusion coefficient of hydrogen, and at $T < 5$ K the local diffusion of hydrogen trapped by nitrogen atoms takes place by under-barrier crossing (tunnelling): under these conditions the hydrogen atom migrates through 16 adjacent tetrapores of the b.c.c. niobium lattice. The nitrogen atoms were shown[41] to be concentrated in the octahedral interstitials of the Nb crystal lattice by the proton channelling method, using the $^{15}N(p, \alpha\gamma)^{12}C$ nuclear reaction.

Thus the diffusional transport of hydrogen along the tetrapores takes place round an octapore occupied by a heteroatom (O or N). Trapping states created by the interstitial atoms must lower the mobility of hydrogen in Nb.

It has been shown[42] that the decrease in mobility of H (or D) in niobium containing up to 1 at.% of nigrogen is most marked at low temperatures (<200 K). The effective diffusion coefficient of hydrogen depends on the concentration of interstitial sites in Nb occupied by impurity atoms:

$$D_H^{\mathrm{eff}} = D_H(\partial c_H^f/\partial c_H) \quad , \tag{8}$$

where c_H^f is the concentration of free hydrogen in the niobium. According to results obtained by an electrochemical method[43] the D_H^{eff} value in interstial alloys with $c_H \geqq 0.03$ wt.% is $(1.80–3.90) \times 10^{-8}$ cm^2 s^{-1}.

It was recently confirmed[44,45] that at low temperatures (0.04–2 K) the trapping of interstial H and D atoms by oxygen impurities in niobium takes place by tunnelling. By measuring the temperature dependence of the specific heat experimental values of the tunnelling matrix elements were calculated by the Flinn–Stoneham theory, and no difference was detected between H and D interstitial atoms for oxygen concentrations ≤2 at.% in the niobium.

The situation in which oxygen is concentrated in the near-surface layer of niobium forming stoichiometric or non-stoichiometric Nb_xO_y compounds is of great practical interest. Extensive information is available on the structure and properties of these oxides. The substantial change in the concentration of hydrogen obtained by saturating niobium foils covered with niobium pentoxide Nb_2O_5 is due to the depletion of hydrogen in the surface layer.[46] These results were obtained by the $^1H(^{15}N, \alpha\gamma)^{12}C$ nuclear reaction, but a calculation of the thickness of the hydrogen-containing layers by an X-ray method gave almost the same result.

The effect of substitutional impurities (V, Ta, Mo) at low concentrations on the solubility of hydrogen in niobium has been studied.[46–50] Substitutional impurities are usually introduced in order to improve the mechanical properties and the inertness of niobium. Thus it was shown[49] that the solubility of hydrogen in Nb is raised by Ta, Mo, and (specially) V impurities. This effect is due to the energetically favourable interaction of H with the substitutional impurity atoms, which increases as the atomic radius of the alloying element is decreased with respect to the Nb lattice parameters (since the H atom decreases the lattice deformation produced by the alloying atom).

The bond energy of the hydrogen in tetrahedral positions round a V atom had been estimated[48] to be $E_{V-H} = 0.09 \pm 0.05$ eV, i.e. close to the bond energy in the complex between hydrogen and an interstitial impurity ($E_{H-O} = 0.09$ eV).[37] However, it was later shown[46] that the energy of the V–H bond has a much lower value (0.04 eV), and that trapping of hydrogen atoms on vanadium impurities in niobium is not normally observed between 2 and 293 K.[50] The probability of self-trapping of hydrogen and deuterium atoms and of μ^+ mesons in Nb crystals containing the substitutional impurities Ti, Cr, and V has been calculated.[51]

Recent experiments with Nb crystals containing substitutional Cr and Ti impurities[52,53] are inconsistent with the theoretical expectation of trapping of the hydrogen atoms mainly as a result of the deformation fields created by the impurities. A more general method, used in Ref.51, includes constructing the potential energy operator for the hydrogen in a suitably averaged crystal field, calculating the zero displacement of the hydrogen by an appropriate three-dimensional form of the Schrödinger equation, and finally evaluating the lattice distortions produced by the insertion of hydrogen (using a set of Green's functions as in calculations for static problems). This method was applied to the self-trapping of hydrogen, deuterium, and μ^+ mesons in Nb crystals containing Ti, Cr, and V substitutional impurities. Comparing the results with experimental data obtained by inelastic neutron scattering showed a generally good agreement: the few discrepancies were attributed to the simplifcations introduced in the calculation.

Of course, a much greater increase in the solubility of hydrogen can be expected in the presence of substitutional impurities from Groups V and VI, such as S, Se, Te, Bi, and Cr. In this case the increase in solubility results not only from the elastic distortions of the Nb lattice but also from the high energy of the bond between the hydrogen atoms and the elements of Groups V and VI.

2. Line Defects

The interaction between hydrogen and dislocations is very important in niobium, because it has a fundamental influence on the mechanical characteristics of the material. Extensive studies of the hydrogen–dislocation interactions have been reported: the most interesting result for b.c.c. metals is the non-conservative motion of the dislocations and the absence of a limited set of slip directions.

Phenomenological discussions of hydrogen–dislocation interactions are usually based on expression of the type of (1); the formation of a Cottrell atmosphere (the atmosphere of impurity hydrogen atoms surrounding the dislocation) can be described by the expression

$$c_H = c_H^0 \cdot \exp(\sigma_H V_H/RT) \quad , \tag{9}$$

where c_H^0 is the equilibrium concentration of hydrogen in the lattice, ν_H is the partial molar volume of hydrogen in the metal, and σ_H is the hydrostatic pressure of hydrogen. Attempts to allow for the dislocation core by the linear theory of elasticity[54] yielded a more complicated form of Eqn.(9):

$$c_H = \pi r_0^2 l c_H^0 \cdot \cosh(\sigma_H V_H/RT) \cdot \exp(\sigma_H' V_H/RT) \quad , \tag{10}$$

where σ_H' is the additional pressure on the dislocation core resulting from the chemical hydrogen–dislocation interaction, l is the length of the dislocation, and r_0 is the radius of the dislocation core (~0.18 nm).

For large c_H^0 Eqns.(9) and (10) should be replaced by Fermi–Diract distribution expressions.[55] In the quantum-mechanical approximation Eqn.(10) contains additional terms for the anisotropic nature of the hydrogen–dislocation interaction; Eqn.(10) should also contain terms allowing for the virtual forces (Kanzaki forces).

The hydrogen–dislocation interaction not only suppresses the mobility of the dislocations but it also affects their concentration, especially near the grain boundaries in a polycrystal. Thus it has been shown[56] that in the electrolytic hydrogenation of polycrystalline niobium the dislocation density ρ increases from 6×10^{11} to 1.3×10^{14} m^{-2} as c_H increases. This increase is attributed[56] to H–H interactions and to the precipitation of a hydride phase at the niobium grain boundaries, which activates a source of dislocations within the grain. A hydride phase can also be formed (at high P_H) directly within the grain, as a result of the inclusion of dissolved hydrogen atoms in clusters and local precipitation of hydride. Hydride formation takes place[57] as a cooperative rearrangement of the crystal lattice in small regions of supersaturated solutions of hydrogen in metals.

The most convincing evidence of hydrogen–dislocation interactions was obtained in studies of the relaxation properties of hydrogenated metals, in which the rearrangement of dislocation structures through reversible mechanical interactions is determined by impurities precipitated at dislocations. Thus a study of the stripping of dislocations from obstacles[58] in very pure polycrystalline niobium at 5–300 K by the internal friction method has shown that at $T < 70$ K the presence of hydrogen atoms leads to the pinning of dislocations. Similar results were obtained[59] at $T < 100$ K for high-purity niobium with a very low concentration of hydrogen ($<10^{-6}$ at.%). The stripping of the dislocations from the anchoring points produces internal friction peaks. The dependence of the vibration frequency of the sample (f) on E_a and on the applied load (σ) is given by the expression

$$f = \nu_0 \cdot \exp\left(-\frac{E_a - \sigma V_a}{k_B T}\right) , \tag{11}$$

where V_a is the activation volume, $\sigma = G\varepsilon_{max}$, G is the normal elastic modulus, ν_0 is the vibration frequency of the dislocations, and ε_{max} is the maximum deformation of the sample. It follows from (11) that decreasing V_a and G produces obstacles to the motion of the dislocations in a hydrogenated crystal. Obviously, this situation will be found in samples supersaturated with hydrogen.

The most detailed studies of the relaxation properties of hydrogenated niobium over a wide temperature range are described in Refs.60 and 61. Two peaks are found on the temperature dependence of the internal friction (Q^{-1}): the first (the α peak) at 123–143 K, and the second (the γ peak) at 263–268 K. In the absence of dissolved hydrogen the magnitude and position of these peaks depend on the extent of deformation of the niobium.[62] Increasing the vibration frequency of the hydrogenated niobium samples (f) from 0.49 to 3.4 Hz results in a degenerate γ peak, while the height of the α peak stays constant. On the other hand the height of the α peak is strongly influenced by the intensity of the preliminary deformation ε, and the signal is highest in the case of an annealed sample. The decrease in height of the peak with increase in f is attributed to hydrogen–dislocation interactions, and to the easier detachment of dislocations from their hydrogen atmosphere at higher frequencies. Allowance for the change in permeability of the dislocation stoppers as a result of hydrogenation is essential in the analysis of dislocation motions. Low-angle boundaries (consisting of dislocation walls) usually behave as strong barriers to the motion of dislocations. However, barriers such as grain boundaries, microscopic inclusions, etc. have an even greater effect.

3. Plane Defects

The changes in physical characteristics produced by the hydrogenation of niobium bicrystal samples are very fully characterised experimentally. It has been shown[63] that an iron bicrystal can be split into individual single crystals by hydrogenation under an applied stress. Large niobium bicrystals can be prepared by electron-beam zone melting,[64] with any required misorientation (δ); the dislocation density ρ in the bicrystal is higher than in a monocrystal grown under the same conditions (the ρ value was determined by measuring electrical resistance at room temperature and at liquid helium temperature).

When determining the rate of corrosion (K) along the boundary of a niobium bicrystal we must allow not only for δ but also for the crystallographic orientation $\{hkl\}$ of the contacting planes of the individual crystals, since the K value for a given plane depends on the $\langle hkl\rangle$ direction. Thus it has been shown[16] that for a $[011]/\langle 0\bar{1}1\rangle$ boundary with $\delta = 16°$ the parameter K along the grain boundary and the extent of corrosion (d_K) go through a maximum; however, the resulting concentration profile is asymmetric because of the difference between the K values for different crystal planes. The dependences of δ on d_K are linear only for $\delta \leq 20°$. Beyond this point non-linearity is observed, and a minimum appears on the plot of d_K against δ for $\delta = 28°$, probably due to a change in the structure of the grain boundary with increasing δ. Whereas the number of coincident sites decreases regularly with increasing δ for small misorientations, when $\delta \geq 20°$ this number can fall away steeply after an initial increase.

Point defects can easily interact with ground boundaries, and therefore very pure bicrystals must be used in studies of the effect of hydrogen. The accumulation of large atoms of the p and sp elements at the grain boundary can greatly distort the structure of the boundary and affect its adsorption properties towards hydrogen. The diffusional mobility of hydrogen moving in the bulk of the grain or along the grain boundary has been calculated.[66] The diffusion coefficient D_H determined electrochemically for grain-boundary diffusion is usually two orders of magnitude greater than for the bulk of the grain.

4. The Surface

The most important defect of a solid is its surface. We have already mentioned the influence of surface oxidation on the absorption of hydrogen by niobium samples. The surface acts as a kind of filter which transmits the adsorbed hydrogen atoms. Therefore even slight contamination of the surface by foreign atoms can seriously alter the energy balance of the adsorption and of the subsequent penetration of the hydrogen into the metal. The largest effects are produced by surface oxygen, or (in the case of electrochemical processes) by water molecules adsorbed by their oxygen atom. A study by electron-stimulated desorption[65] has shown that oxygen adsorbed on the (110) and (100) niobium surfaces can be desorbed by H^+ ions. The ability of H^+ to desorb oxygen by the electrochemical reaction $H^+ + MO + \bar{e} \rightarrow 2M + OH$ depends on the crystallographic indices of the plane: the rate of desorption is lower on the less densely packed (111) plane.

The most widely used method of protecting the surface of the metal to be hydrogenated from oxidation is to deposit a layer of a noble metal (for example, palladium). This is often done in studies of the hydrogen permeability of membranes. However, we must allow for the change in the electronic structure of both metals resulting from the formation of the Pd/Nb contact.[67] A large decrease in the density of *d* states of Nb at the Fermi level (E_F) after the adsorption of palladium was noted in a study of the (110) surface of the Pd/Nb contact. A decrease in the density of *d* states should lower the solubility of hydrogen in a transition metal, since the absorption of hydrogen is accompanied by interaction of the hydrogen *s* electron with the *d* band of the metal.

The hydrogen can exist in two types of bound state on the crystal surface (in other words, the energy level of the surface has two minima). In the case of one-centre adsorption on the first layer of atoms (*r*-type adsorption) the bond between H_{ads} and the surface is weaker. Hydrogen in the *r* form can diffuse along the surface, and it can form planar adsorbed structures with various periodicities on the billiard-ball packed (110) niobium surface. Hydrogen in the *s* state (in the second layer of surface atoms) is more strongly bound. In this case the less closely packed {111} surfaces can more readily form hydrogen structures in the *s* state. The rate at which an adsorbed hydrogen atom is transferred into the *s* state depends on the pressure of hydrogen on the metal surface. For monocrystalline samples the rate of crossing of the interfacial boundary by adsorbed hydrogen atoms is strongly dependent on (*hkl*), and the hydrogenation kinetics are determined by the combined processes at the surface and in the bulk of the niobium lattice. The contribution of the surface processes on the (110) niobium surface was found[68] to be predominant.

When the Nb surface is covered with oxygen the desorption of oxygen by hydrogenation should be easiest on the close-packed (110) surface and least effective on the (111) face. On the clean surfaces which can be produced by lengthy desorption treatment during hydrogenation the spin–spin interaction between the adsorbed hydrogen atoms cannot be ignored. The recombination and desorption of the hydrogen atoms from the surface take place most readily in the case of antiparallel spins.

V. CHANGES IN THE PHYSICO-MECHANICAL CHARACTERISTICS OF NIOBIUM CAUSED BY HYDROGENATION

The interaction of hydrogen with point and line defects and with grain boundaries and matrix atoms (hydride formation) produces a change in the physico-mechanical properties of the metal often accompanied by large-scale mechanical failure, even without externally applied loads. Thus it was reported[69,70] that the saturation of very pure rolled niobium with electrolytically generated hydrogen caused embrittlement of the sample. With Nb samples in wire form (0.3 mm diameter) containing $c_H \geqq 0.03$ wt.% of hydrogen the onset of hydrogen embrittlement (which depends on the extent of the previous deformation ε) was found to be associated with the formation of a hydride phase. The hydrogen embrittlement increases for $\varepsilon \leqq 5\%$, but as ε is further increased from 5 to 98% the embrittlement decreases. This has been attributed[70] to the formation of a cellular dislocation structure at high values of ε, whose rearrangement is hindered during hydrogenation.

Combined metallographic and X-ray diffraction studies[70] explained these changes in the mechanical properties of niobium as due to reversible distortions of the crystal lattice of the matrix during the first and the second hydrogenation stage, and to the formation of a hydride (Nb_xH_y) with a larger lattice constant during the third stage. Since its specific volume is greater than that of the matrix the hydride is concentrated along certain crystallographic directions <*hkl*> and produces large stresses (sufficient to cause spontaneous fracture of the metal when c_H is increased).

In some of the most detailed studies of hydrogen embrittlement[71,72] the effect in the Nb–H alloys was also associated with dislocation effects, resulting from the formation of hydride particles (precipitates) at the extremities of the resulting cracks. The hydrogen cracking is produced by the high internal stresses generated in the metal, and the hydride particles act as foci for the generation of breakdown, giving a high plasticity to the Nb–H alloys with a uniform distribution of particles. A study of the hydrogen embrittlement of niobium samples stretched within the column of the electron microscope showed that no embrittlement takes place at low c_H values, as also found in earlier investigations.[69]

A simple relationship between the increase in length of the hydrogen cracks $\Delta\tau_H$ and the characteristics of the hydrogen precipitates (hydride particles) has been reported:[73]

$$\Delta\tau_H = \frac{\pi r_B \gamma_0}{2bl_B}, \qquad (12)$$

where *b* is the Burgers vector of the dislocation, l_B is the distance between the hydrogen precipitates, r_B is their radius, and γ_0 is the surface energy of the hydrogen precipitate.

The hydrogen–dislocation interaction determines the growth of the crack during loads with an alternating sign, i.e. in the most hazardous conditions experienced in the practical application of niobium components operating in hydrogenating media. Experiments with foil samples of Nb at 293 K and a load cycling frequency of 4 Hz showed[74] that the liability to catastrophic breakdown increases with c_H.

In polycrystalline material the hydrogen embrittlement is strongly affected by impurities which can react chemically with hydrogen, as was stated above. Contamination of the niobium with oxygen or nitrogen (~0.1 at.%) raises the critical embrittlement temperature: the Porteven–Le Chatelier effect is clearly seen at 340–394 K in oxygen-containing samples[75]. It is due to the suppression of the motion of dislocations by the oxygen (Snoek) atmospheres. The interaction of oxygen with hydrogen should strongly influence this effect, partly because the hydrogen–dislocation interaction tends to retard the motion of dislocation in the hydrogen-saturated lattice, and partly because the increased mobility of the oxygen atoms in an anisotropically distorted hydrogenated lattice tends to oppose the effect.

The substitutional impurities V, Mo, and Ta (~3–5 at.%) have a dominant effect on the solubility of hydrogen (P_M) in niobium.[49] Vanadium impurities increase P_M most strongly, possibly because the interaction of hydrogen with substitutional impurities having a radius smaller than niobium is energetically favoured.[76] In this case the hydrogen decreases the deformation of the lattice. However, as was pointed out above, these systems (unlike those containing interstitial impurities) do not show direct M–H chemical interaction.

The effect of the distribution of impurities on the hydrogen embrittlement is stronger in polycrystalline than in monocrystalline samples.[76] For identical c_H values the differences in mechanical properties under tension between mono- and polycrystalline niobium samples are observable at 291–295 K, and the minima on the temperature dependences of the mechanical characteristics and of the internal friction are in similar positions. This is evidence that the hydrogen–dislocation interaction is responsible for the change in mechanical characteristics. The maxima in the temperature dependence of the mechanical characteristics near 300 K are also close to the maxima which characterise the γ peaks on the internal friction curves. Electron fractograms of the fracture surfaces of Nb mono- and polycrystals revealed fragmentation and cellular break,[7] typical of polycrystalline samples, at high c_H values. The formation of a "river pattern" on the fractogram in the presence of hydrogen embrittlement distinguished most of the tests at low temperatures (77 K).

Thus the change in mechanical characteristics of niobium is due to the rearrangement of the metal structure at a number of levels, initiated by the hydrogenation.

VI. ELECTROCHEMICAL ASPECTS OF THE PROBLEM

Let us now examine the corrosion-electrochemical behaviour of niobium in various electrolytes and the role in these processes of structural changes induced by hydrogenation.

1. Kinetics and Mechanism of the Corrosion-electrochemical Processes on a Niobium Surface in Acid Media

Electrochemical studies of niobium in acid media were begun only recently. Most of the published data refer to changes in the hydrogen overvoltage (η) on niobium in acid media. This is because niobium and its alloys are promising new materials for the electrolytic production of hydrogen by electrolysis of aqueous solutions. The dependence of the potential of an oxidised niobium electrode at 298 K on the pH of the solution can be expressed as

$$\varphi = \varphi^0_{Nb_2O_5/Nb} - 0.0591\,\mathrm{pH}\ , \tag{13}$$

which shows that this system can be used as an indicator electrode.[77] The equilibrium potential of the system in buffer media of pH ~ 2 is established in 15–20 min. It is reported[77] that after mechanical polishing or anodic surface treatment the niobium electrode can be used for potentiometric redox titrations in solutions of pH $\leq$ 10. The exact reversibility of the Nb–H binary system during hydrogenation cycles allows the Nb electrode to be used as an electrothermal resistor.[78]

The anodic characteristics of niobium (a valve metal whose oxide has semiconductor properties) and those of its alloys have been less extensively studied. The anodic oxide, as was stated above, plays a controlling role in metal–electrolyte exchange processes. Studies of Nb and Ni–Nb in the amorphous and the crystalline state have shown[79] that a defect-free oxide film having a high electronic conductivity is formed on the amorphous alloy. This allows the $Ni_{60}Nb_{40}$ alloy to exist in a stable passive state. In acid solutions niobium is easily passivated by anodic polarisation. According to Heusler[80] the stationary corrosion of Nb in the passive state is controlled by the structure of the oxide and depends on its rearrangement and erosion. The reforming of the oxide layer by electrochemical treatment is attributed[81] to the transport of ionic defects such as uncoordinated metal and oxygen atoms. These defects are formed on the metal–oxide and oxide–electrolyte interfaces, and their transport in the oxide layer takes place by the switching over of broken bonds on the metal and oxygen atoms.

In recent years Nb has been used in alloy making not only as a carbide-forming additive but also as a major component to assist austenitic grain growth and to give enhanced passivation.[82–86] As the Pourbaix diagram of the niobium–water system shows, oxide films on the niobium surface are unstable in alkaline solutions, and the niobium should corrode rapidly. Oxygen-covered Nb surfaces are strongly affected by anions (SO_4^{2-}, halides) and by surface-active species, which produce changes in the Nb–O bond energy. Thus, sulphur deposited on the niobium surface weakens the bond between adsorbed oxygen atoms and the surface very substantially. This can be explained[87] by assuming that the adsorption centres for oxygen and sulphur are the same.

Thus on the oxidised surface of a Nb electrode the adsorption of hydrogen is to a large extent reversible. The reversibility can be disrupted by the adsorption of anions from the electrolyte or of hydride-forming elements. Complete dissolution of the niobium oxide Nb_xO_y is possible only in a cathodic process far removed from equilibrium.

2. Electrochemical Characteristics of Niobium in the Cathodic Potential Region

Some of the earlier work[88–90] dealt with the hydrogen overvoltage on niobium and showed that the dependence of η on the cathodic current i_K and on the pH can be described by the slow discharge theory. For i_K = const we observe a strong time dependence of the potential ϕ: stabilisation occurs after 3 applications of cathodic polarisation lasting 1 h each. This is due mainly to the reduction of Nb_xO_y thin films during cathodic polarisation.

According to the polarisation measurements the nature of the alkali (NaOH, KOH, LiOH) has practically no effect on the overvoltage (unlike the concentration of the electrolyte).[90] Since the free energy of adsorption of atomic hydrogen on niobium is high, the hydrogen evolution reaction is rate-limited by the electrochemical desorption step:

$$H_2O + \bar{e}(M) \rightleftarrows H_{ads}M + OH^- \tag{14}$$

$$H_2O + \bar{e}(M) + H_{ads}M \rightarrow 2M + OH^- + H_2 \tag{15}$$

At surface coverages of the Nb by atomic hydrogen $\theta_H \cong 1$ the overvoltage equation is

$$\eta = k_{15} - \frac{1-\alpha}{\alpha} \cdot \frac{RT}{F} \ln a_{H_2O} - \frac{RT}{F} \ln a_{OH^-} + \frac{RT}{F} \ln i_K \tag{16}$$

where a_{H_2O} and a_{OH^-} are the activity of water and of the hydroxyl ion respectively, F is the Faraday, α is the transfer coefficient, k_{15} is the rate constant of reaction (15), and R is the gas constant.

This equation is accurately consistent with experimental data:[91] the dependence of η on $\ln [a_{H_2O}^{\frac{1-\alpha}{\alpha}} \cdot a_{OH^-}]$ is linear, with a slope (b_K) close to the theoretical value. A discontinuous change in hydrogen overvoltage on niobium resulting from previous cathodic treatment of the surface has also been reported,[88–90] and attributed to the discrete change in lattice constant caused by hydrogenation and hydride formation. After lengthy hydrogenation (30 h at i_K = 100 A m^{-2}) the lattice constant a becomes stable, resulting in a steady value of η; at higher values of i_K the changes in η are more rapidly suppressed.

A study of the electrochemical properties of the interface between niobium and a sulphuric acid electrolyte showed[89] that as a result of cathodic polarisation the double-layer capacitance (C_d) on Nb rapidly rises (in 0.5 h for i_K = 100 to 250 A m^{-2}) from 50–60 to 80 μF cm^{-2}. This increase is attributed[89] to the reduction of the thin oxide layers formed on the metal as a result of previous anodic treatment rather than to phase transitions in the near-surface layer of Nb. The micro-hardness *HV* of hydrogenated Nb layers gradually increased, reaching a stable value 10–15 h after the beginning of the cathodic polarisation, which is consistent with the X-ray analysis results. Sudden changes in current (oscillations) in alkaline solutions are well known in efficiently passivated 4*d* metals. In this case the kinetic equation for the hydrogen evolution reaction becomes

$$i_K = i_0 \cdot \exp\left[-\frac{(1-\alpha)F\eta}{RT}\right] \tag{17}$$

where i_0 is the exchange current. The oscillations of i_K often observed at high values of η are associated with ohmic changes in the near-electrode layer, i.e. with oscillations in the resistance of the electrolyte layer resulting from the alternate accumulation of molecular hydrogen and of Nb^{3+} ions.[92]

A calculation of the activation energy of the dissolution of hydrogen in Nb in H_2SO_4 solutions by Gorbachev's temperature-kinetic method gave values of 44.0 [88,89] and 47.3 kJ mole^{-1}.[93] In this case the hydrogen evolution corresponds to the Volmer process

$$H_3O^+ + \bar{e}(M) \rightleftarrows H_{ads}M + H_2O \qquad (18)$$

Thus the kinetics and mechanism of the hydrogen evolution reaction on a Nb electrode surface are very dependent on the formation of a hydride phase in the near-surface layer. The mechanism of the elementary act is complicated by the change in electronic structure of the surface on which the hydrogen is adsorbed. The overvoltage of the hydrogen evolution reaction on the hydride depends on the degree of saturation of the near-surface layer with hydrogen and on the intensity of the cathodic process.

A recent review[94] discusses three possible mechanisms of the hydrogen evolution reaction on niobium. The first includes the Volmer process (18), which determines the rate of evolution of hydrogen, followed by the fast step (Heyrovsky–Horiuti process)

$$H_{ads}M + H_3O^+ + \bar{e}(M) \rightleftarrows 2M + H_2 \qquad (19)$$

The second mechanism consists of the fast Volmer reaction (18) followed by the slow step (Tafel process)

$$H_{ads}M + H_{ads}M \rightleftarrows 2M + H_2 \qquad (20)$$

This mechanism is controlled by the recombination of H_{ads}, and therefore the rate of hydrogen evolution is independent of the electrode potential. The third mechanism postulates a fast Volmer reaction (18) followed by a slow Heyrovsky–Horiuti reaction (19). In this case the cathodic current is described by the expression

$$i_K = k_c a_{H_3O^+} \cdot \exp\left[-\frac{(1-\alpha)F\varphi}{RT}\right], \qquad (21)$$

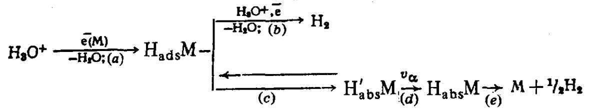
where k_c is the rate constant and $a_{H_3O^+}$ is the activity of H_3O^+. According to Eqn.(21) the slope of the polarisation curve is $(\partial\phi/\partial \lg i_K)_{pH,T} = 2.3RT/(1-\alpha)F$, and the order of the reaction with respect to OH^- ions is $(\partial \lg i_K/\partial\, pH)_{\phi,T} = 1$. These parameters apply to both polycrystalline and monocrystalline samples.

The adsorbed hydrogen can either be evolved from the metal surface or be transferred to an internally adsorbed state under the M electrode surface (*s* form), from which it can redistribute itself in the near-surface layer by diffusion:[95]

$$H_{ads}M \underset{k_{ads}}{\overset{k_{abs}}{\rightleftarrows}} H_sM \qquad (22)$$

Here k_{abs} and k_{ads} are the rate constants for the absorption of hydrogen by the metal and for its adsorption on the surface from the bulk of the metal.

In general the cathodic process leading to hydrogen evolution in acid media can be expressed as follows:[95]



$$H_3O^+ \xrightarrow[-H_2O;\,(a)]{\bar{e}(M)} H_{ads}M - \left| \begin{array}{l} \xrightarrow[-H_2O;\,(b)]{H_3O^+,\,\bar{e}} H_2 \\ \\ \xleftarrow{\hspace{3em}} \\ \xrightarrow[(c)]{\hspace{3em}} H'_{abs}M \xrightarrow[(d)]{v_\alpha} H_{abs}M \xrightarrow[(e)]{} M + {}^1/_2H_2 \end{array} \right. \qquad (23)$$

Here ν_α is the diffusional flow of hydrogen atoms into the bulk of the metal; $H'_{abs}M$ and $H_{abs}M$ denote an absorbed hydrogen atom on the metal surface and under it respectively. Some of the hydrogen forms molecules and emerges into the electrolyte, whereas the remainder penetrates into the metal where it can either form a solid solution or be bound in a hydride phase. It was suggested[69] that step (*c*) in Eqn.(23) is at equilibrium, i.e. that the hydrogen adsorbed in the *s* state is removed by electrochemical desorption according to Eqn.(19). In the case of the hydrogen absorbed by the metal two situations can arise: 1) the whole of the absorbed hydrogen is present in the bound (hydride) form, or 2) a chemical M–H bond is not formed, and supersaturation of the near-surface layer initiates the desorption process [step (*e*)], in which the hydrogen is returned to the metal–electrolyte interface where it undergoes electrochemical desorption by reaction (19).[96] Lastly, these two processes can occur simultaneously, producing a quasi-equilibrium state characterised by the slow breakdown of the hydride layer with evolution of hydrogen at the metal–electrolyte interface. We should stress that the hydrogen in solid solution is not desorbed from the entire surface of the metal but only from some specific active centres (usually, line or plane defects on the metal surface).

In the formal kinetic treatment of the scheme (23) the ratio of the rates of certain steps should affect the overall balance of hydrogen absorbed by the metal and hydrogen removed electrochemically. Experimental data for the hydride-containing metal agree well with mechanism of hydride layer formation followed by binding of the absorbed hydrogen in the hydride. In a hydrochloric acid solution the parameter b_K increases as a result of hydrogenation.[88,89] A study of the frequency dependence of the impedance[89] suggests that step (c) could be treated as a heterogeneous chemical reaction.

The general conclusion from this Section is that for low c_H in the near-surface layer (and correspondingly short cathodic polarisation times) the rate of the hydrogen evolution reaction is controlled by the slow discharge step (18). For longer cathodic processes (i.e. for high levels of hydrogenation) we must allow for the formation of Nb–H chemical bond, the decrease in the Fermi energy E_F, and the "ennoblement" of the metal resulting from the filling of the *d* band of the transition metal by the *s* electrons of the hydrogen. The decomposition of the supersaturated solid solution or the dissociation of the Nb_xH_y hydride influences the electrochemical process on the metal surface, causing an increase in the rate of formation of hydrogen molecules and possibly also in the rate of electrochemical desorption of the hydrogen.

3. Electrochemical Characteristics of the Niobium Electrode During Anodic Polarisation

Let us now examine the anodic process coupled with the hydrogen evolution reaction. The main process during anodic polarisation is the formation of an oxide layer on the anode. The initial stages of the reaction of oxygen with a clean monocrystalline niobium surface were studied[97] by a molecular beam method, which gave the changes in the sticking coefficient of the oxygen atoms (the ratio of the total number of sorbed oxygen atoms to the number of metal surface atoms on the (110) niobium face) as a function of θ_H and T. The adsorption of oxygen on the (110) face was shown to be a complex, multi-stage process, controlled by the diffusion of oxygen atoms into the bulk of the crystal. Thus on the most densely packed (110) face of niobium the adsorption of oxygen in the *s* state is possible only at high coverages of the surface by oxygen (θ_0), and its requires cooperative lateral displacements of the first layer of Nb atoms. At low θ_0 values a very thin ($l \cong 0.5$ nm) layer of oxide (Nb_xO_y, $x = 1$, $y \leq 1$) is first formed on a clean polycrystalline or monocrystalline Nb surface at 293–295 K, and this initial layer is converted into Nb_2O_5 when $l > 2$ nm.[98]

The growth of oxide films showing ionic conduction in electrolytes under anodic conditions is the result of a chemical diffusion process in an oxide of non-stoichiometric composition. Ionic transport in the growing oxide layer has been attributed[81] to the motion of positive or negative NbO_2^+ and NbO_2^- ions by the "switching over" of broken bonds on the oxygen and niobium atoms. The NbO_2^+ ions are formed at the metal–oxide interface, and the NbO_2^- ions at the oxide–solution interface. The kinetics of the formation of a layer of oxide on the anode are determined to a large extent by external conditions in the electrolyte (parameters of the anodic treatment, pH and concentration of the solution).

After a long cathodic treatment a layer of hydrides is formed on the niobium surface by the percolation mechanism. This process is hindered by non-uniform reduction of the oxide layer. An ellipsometric study[99] of changes in oxide films formed in air or by anodic oxidation of a niobium electrode, and of changes in the hydride layer previously formed by cathodic treatment over a wide range of electrode potentials, has been reported.

A study of the formation kinetics of anodic oxide on niobium by the capacitance method[100] in dilute solutions of salts, acids, and bases has shown that the formation potential of the oxide (ϕ_{ox}) is linearly time-dependent at 293–333 K. It was established[100] that under conditions of 100% current yield the thickness l of the oxide film increases according to the Young equation

$$l = k\varphi_{ox} \tag{24}$$

during the anodic oxidation, and that the rate constant of the formation $k = 2.6$ nm V^{-1} depends on the temperature and on the anodic current density i_a. Anodic polarisation of a Nb electrode covered with a layer of hydrides results in dissociation of the hydrides and formation of a new oxide layer. Cathodic polarisation of a Nb electrode bearing an anodic oxide layer does not immediately regenerate a layer of hydrides under the oxide layer. According to Auger spectral results a thin oxide layer may persist over the hydride layer even after lengthy cathodic treatment.[99] The rearrangement of the anodic oxide during hydrogenation has been interpreted[101] as an electron–proton reaction with a decrease in the valency of Nb:

$$Nb_2O_5 + H_3O^+ + \bar{e} \rightarrow Nb_2O_4OH + H_2O \tag{25}$$

The intermediate formed by reaction (25) is characteristic of the anodic treatment of Nb in alkaline solutions, since the discharge of hydrogen ions during the cathodic process increases the electronic conductivity of the Nb_2O_5 oxide: in these circumstances we must also allow for the electron-acceptor nature of the Nb^{4+} ions.

Anodic oxidation of a Nb electrode in alkaline KOH solutions leads to the formation of niobium dioxide NbO_2 as well as Nb_2O_5 on the surface.[102] Shatalov and co-workers[103] formed anodic oxides in 1 *N* solutions of HCl, HNO_3, H_3PO_4, and H_2SO_4, and they showed that the polarisation of the Nb electrode increases with time for a constant i_a. The most perfect anodic oxide layer was formed in a phosphoric acid solution, where the high electric fields needed to enhance the protective action of the Nb_xO_y are produced by changes in E_a rather than by the penetration of PO_4^{3-} into the oxide layer. However, the anionic composition of the solution during the anodic polarisation of niobium has a marked effect on the chemical composition of the anodic oxide layer. It has been reported[104] that the anodic layer produced in a 10 M H_3PO_4 solution at $i_a = 10^4$–10^6 A m^{-2} contains phosphorus impurities (up to 95 gm cm^{-2}). The partial inclusion of PO_4^{3-} ions in the anodic oxide layer is probably responsible for its high structural perfection. The anodic dissolution process is fastest in solutions containing F^- ions, since under these conditions the oxygen in the anodic layer is replaced by F^- (which has a higher affinity for Nb). The rate of dissolution of niobium fluorides is also high.

Some interesting aspects of the anodic behaviour of the $Nb_{25}Ni_{75}$ alloy in sulphuric acid solutions were observed in that work.[104] Separately, both nickel and niobium readily dissolve in sulphuric acid solutions containing halide ions (Hal^-) under anodic polarisation. However, their alloy is rapidly passivated in the same solutions. It is suggested[104] that the Nb atom is oxidised while still in the metal lattice, which lowers its activity (since NbO_2^+ has a low activity), so that the atom does not go into solution but is retained on the surface, forming a passivating oxide film. This film consists of a mixed oxide whose composition and properties are determined by the corrosion-kinetic characteristics of the components.

Alloying the niobium with noble-metal additives should make the passivating oxides chemically even more unreactive and should lower the rate of the anodic process.[105] Adding the Cl^- ion to the electrolyte increases i_a. Adding C_2H_5OH to an acid aqueous solution containing Hal^- ions lowers the number of activating anions which are adsorbed and incorporated into the anodic oxide film.[106] Accordingly, the addition of water to alcoholic bromide solutions increase the rate of the active dissolution of Nb, whereas the addition of C_2H_5OH to aqueous solutions suppresses it. A totally passive state of the Nb electrode can be obtained at some well defined ratios of alcohol to water.

The rate of anodic dissolution is very dependent on the pH. It was shown[107] that at pH > 11.3 the current i_a is almost independent of the concentration of ions ($c_{H_3O^+}$). The process is controlled by reactions (14) and (15), and its rate at $\theta_H \to 1$ can be calculated by Eqn.(21).

Thus during the formation of an anodic oxide layer the anions present in solution (especially Hal^- ions) can penetrate into the layer and affect the corrosion resistance of niobium and its alloys. The chemical affinity of the anion from the solution towards niobium is mainly responsible for determining the corrosion resistance of the metal in aggressive media: the chemical resistance of Nb can be increased not only by bulk doping but also by surface doping with cathodic additives. The near-surface layers of anodically treated Nb can be doped from acid solutions containing Mo, W, Cr, or Zn impurities, which enhance the protective action of the anodic oxide layer on Nb.[108]

4. Corrosion Behaviour of Niobium in Acid Media

Relatively few experimental results on the corrosion behaviour of niobium and its alloys in aggressive media have been published. In a study of the corrosion of Nb in aqueous hydrochloric acid solutions[109] the rate of corrosion *K* was found to decrease with time. When the temperature is raised from 305 to 373 K the parameter *K* initially increases about 20-fold, but 60 days after the beginning of the corrosion process *K* becomes almost independent of *T* (10 µm day^{-1}). In this temperature range Nb was classified as an absolutely stable metal in 1 *N* HCl solution.[109] The activation energy for dissolution in the HCl/Nb system is 50–90 kJ $mole^{-1}$. The changes in physico-mechanical and corrosion-electrochemical characteristics of Nb caused by hydrogenation without formation of hydride phases do not markedly affect the corrosion resistance of niobium in media of pH > 1, and they may even increase it slightly.[110]

The corrosion resistance of binary alloys based on niobium and of alloys doped with cathodic additives can be much higher than that of pure Nb. Thus a study[111] of the corrosion resistance of binary Nb–Ta alloys has shown that in H_2SO_4, HCl, and HNO_3 solutions these materials are in a passive state over a wide range of potentials and temperatures (373–523 K). This result was subsequently confirmed.[112] The corrosion stability of Nb–Ta alloys can be increased by high-temperature heat treatment, which produces a mixture of Nb and Ta pentoxides on the surface. The chemical inertness of β-Ta_2O_5 containing Nb is substantially higher than that of β-Nb_2O_5 containing Ta. Up to 50 at.% of niobium can be added without significantly impairing the corrosion resistance of tantalum.[112] By additionally doping these alloys with palladium or platinum we can produce constructions materials for the protection of systems operating in very corrosive media.

The corrosion resistance of niobium alloyed with ruthenium and molybdenum is discussed in Refs.113 and 114. Alloying with ruthenium lowers i_a and widens the region of potential in which the passive state is preserved. Measurements of the weight loss of these alloys in 1–10 *N* solutions of H_2SO_4 have shown that the rate of corrosion is extremely low: 10^{-4} mm $year^{-1}$ (~3×10^{-4} μm day^{-1}).[113] Thus the corrosion stability of niobium and its alloys in hydrochloric acid solutions is slightly worse than in sulphuric acid solutions. This is due to the effect of Hal^- ions on the structure and properties of the oxide films on niobium; the SO_4^{2-} ion has a very much lower surface activity.

The rate of corrosion of niobium can be decreased by alloying it with 5–10 wt.% of molybdenum or tungsten. In 4% H_2SO_4 $K = 2.2$ g m^{-2} h^{-1} for pure niobium, and 0.2–0.4 g m^{-2} h^{-1} for Nb–Mo and Nb–W alloys. However, these binary alloys have a low plasticity and require additional alloying. The addition of small quantities of zirconium (0.003–0.1 wt.%) worsens the plasticity but further improves the corrosion resistance by producing oxide layers with a more perfect structure.

The Zr + 2.5 at.% Nb alloys, whose corrosion resistance has been extensively studied,[116] is widely used in nuclear energetics and in various branches of technology. These concentrations of niobium produce a significant loss of corrosion resistance in the zirconium. Furthermore the ease of hydrogenation decreases in this alloy. Thus the Zr + 2.5 at.% Nb has some advantages over the Zircalloy-1 and Zircalloy-2 materials from the point of view of hydrogen embrittlement, but its chemical stability is inferior. This is because of the structural aspects of the oxide films discussed above. The search for effective corrosion inhibitors for this alloy is now an important problem.

5. Effect of Anions from the Solution on the Corrosion Behaviour of Niobium in Acid Media

The Hal^- ions have the strongest influence on the structure of the passivating niobium oxide layers. The passivating film is "infected" by the activating halogen ion,[116] and this lowers the active dissolution potential. Several studies of these processes have been reported, and the F^- ions are invariably found to be the most active depassivators of all the halide ions.

In the anodic dissolution of niobium in sulphuric acid electrolytes containing HF additions the following chemical and electrochemical processes on the anode have been suggested:[117–119]

$$Nb \xrightarrow{n\bar{e}, H_2O} Nb_2O_n \xrightarrow{HF} H_2NbO_xF_{(7-x)} \xrightarrow{HF, H_2SO_4} HNbF_6 , \quad (26)$$

with *x* decreasing from 7 to 0 with increasing distance from the metal surface. It follows from (26) that a film of niobium oxide fluoride is formed on the Nb electrode surface. Its formation is accompanied by oscillations of the current in the anodic polarisation curves. The parameter *n* varies between 4.65 and 4.95, i.e. non-stoichiometric niobium oxides (with poor dielectric properties) are formed. The formation of a layer of Nb_2O_5 depends on the rate of supply of oxygen to the electrode surface and requires currents higher than the limiting current. In media containing Hal^- the cathodically activated Nb electrode dissolves more rapidly. The previous cathodic polarisation increases the pH of the layer of solution adjacent to the cathode and thus helps the formation of an oxide structure more permeable to cations, resulting in a rapid decrease in *K*.[120]

In acid media Cl^- ions cause a loss of dielectric properties in the surface anodic oxides of niobium, obviously through the replacement of O by Hal^- in the film. The effectiveness of the discharge of Cl^- ions on the surface of the $Ni_{60}Nb_{40}$ alloy is increased by amorphisation of the alloy, which thus increases the chemical stability of the alloy in chloride solutions.[81] Anodic polarisation of niobium in a hydrochloric acid solution containing 0.05–10 mole $litre^{-1}$ of Cl^- lowers the effectiveness of the growth of the oxide film, the depassivating action of the adsorbed Cl^- ions being suggested[121] as an explanation.

The multi-step character of the dissolution of niobium is pointed out in many papers. The most obvious manifestations are the rearrangements in the anodic oxide layers on standing, caused by the desorption of electrolyte species. More complex electrochemical systems, containing various organic molecules in addition to solution anions, suppress the activation of niobium in Hal^- ions.[106,122] Thus, Br^- ions in aqueous solutions containing CH_3OH result in the formation of soluble $[Nb(OCH_3)_mBr_n]^{p+}$ complexes. The adsorption of organic molecules (for example, corrosion inhibitors) decreases the incorporation of active halide ions in the anodic oxide layer and thus it also lowers the constant *K*.

Thus halide ions can produce local depassivation of the Nb surface, which can take place on active centres with a low adsorption energy. The practical importance of this effect is obvious, since the great majority of assemblies, components, and apparatus used in the chemical industry are exposed to hydrogenating media containing halogen ions.

The decrease in the corrosion resistance of niobium and its alloys is strongly dependent on structural changes in the passivating oxide layer, which is itself determined by the distortion state, the concentration, and the topology of the defects in the near-surface layer, and by the crystallography of the corroding surface. Hydrogenation not only assists the dissolution of the oxide layers but also induces substantial disorder in the near-surface layer, resulting from the active interaction of the hydrogen with the defects in the metal. Further theoretical and experimental studies of the rearrangement of the surface as a result of hydrogenation and phase transitions in the near-surface layers are needed.

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Modern Ideas About the Processes Involving the Formation and Growth of the Nuclei of a New Phase Under Potentiostatic Conditions

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The principal advances in the theory and practice concerning the initial stages of the electrocrystallisation of metals are considered. The thermodynamic and kinetic relations for the phase formation processes in electrochemical systems and the influence of the kinetics of the discharge of ions and of the adsorption of surfactants on the stationary rate of nucleation are analysed. The theories of the non-stationary nucleus formation and models taking into account the growth of the nuclei of a new phase are discussed.
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I. INTRODUCTION

The study of the mechanism of the formation and growth of the nuclei of a new phase in the electrodeposition of metals is of great theoretical and practical importance, because many properties of galvanic coatings are established precisely in the initial stages of the process. The development of modern technology requires the formation of thin non-porous current conducting, magnetic, and protecting layers and this is possible only on the basis of a careful study of the characteristics of the formation of a new phase.

A series of reviews and monographs have been published in recent years[1-10] in which the theories of homogeneous and heterogeneous nucleus formation have been analysed in detail. Phase formation under galvanostatic conditions has been studied.[11-28] The interpretation of the results obtained in the study of the electrocrystallisation of silver,[11,12,16] cadmium,[13] tin,[15] copper,[23-25,28] and zinc[26,27] under galvanostatic conditions is complicated by the fact that the systems enumerated, which determine the thermodynamics and kinetics of nucleation, vary in accordance with complex laws; the phase formation process is accompanied by a parallel process in which the electrical double layer is charged, part of the current is consumed on the growth of the nuclei already formed, and the ohmic potential drop can reach a considerable magnitude. The theory of galvanic nucleus formation proposed in a number of studies[13,14,17-22] involves, by virtue of the causes enumerated above, many assumptions, which complicate an adequate description of the real processes. In the present review we shall therefore consider mainly the latest theoretical and practical advances in the electrochemical nucleation of metals applicable to potentiostatic conditions.

II. THERMODYNAMICS OF THE FORMATION OF THE NUCLEI OF A NEW PHASE

The phase formation theory was initially developed for homogeneous systems, for example for the process involving the formation of a drop of liquid from a supersaturated vapour.[2,29-31] The change in the free energy of the system ΔG on formation of the nucleus of a new phase, which is equal to the work of nucleation, consists of the changes in the volume and surface energies:

$$\Delta G=-n\Delta\mu+\varphi(n)=-\frac{4\pi r^3\Delta\mu}{3V}+4\pi r^2\sigma ,$$

where n is the number of atoms or molecules in the nucleus, r the radius of the nucleus, $\phi(n)$ its surface energy, σ the specific surface energy at the vapour/liquid boundary, V the atomic or molecular volume, and $\Delta\mu$ the difference between the chemical potentials of the supersaturated and equilibrium vapours, i.e. the degree of supersaturation of the system.

The dependence of the work of formation of the drop on its radius is represented by a curve with a maximum,[2] which corresponds to the critical size of the nucleus, for the given degree of supersaturation, defined by the Gibbs–Thomson equation:

$$r_{cr}=2\sigma V/\Delta\mu \tag{1}$$

Drops with a radius $r < r_{cr}$ tend to dissolve spontaneously, while nuclei with a radius $r > r_{cr}$ tend to grow by virtue of favourable thermodynamic factors. With increase of the degree of such supersaturation in the system, the critical size of the nuclei and the work of their formation diminish and the $\Delta G(r)$ curve shifts to the origin of coordinates.

Using Eqn.(1), it is possible to formulate an expression for the rate of nucleation:[2]

$$\Delta G=\frac{16\pi\sigma^3V^2}{3\Delta\mu^2}=\frac{1}{2}n_{cr}\Delta\mu , \tag{2}$$

where the superscript "cr" corresponds to the critical state.

The critical nucleus can be defined in several ways. It is an aggregate of a new phase, which corresponds to one of the following conditions:

(1) It is in a state of metastable equilibrium with the supersaturated parent phase;

(2) its size is such that the probability of further growth is equal to the probability of dissolution;

(3) on fluctuation-induced formation, it requires the consumption of maximum work.

Within the framework of classical nucleation theory, which operates with continuous quantities, namely the size of the nucleus and the work of its formation, these three definitions are equivalent.[32]

Heterogeneous nucleus formation has been examined in a series of studies.[1,2,6,29,31,33] The formal theory presupposes that the nucleus of a liquid on the surface of a solid support has the form of a spherical segment and the change in the energy of the system ΔG^{het} following its formation is proportional to the work of homogeneous nucleation ΔG^{hom}:

$$\Delta G^{het} = \Phi \Delta G^{hom}, \tag{3}$$

where Φ is the shape factor which is equal to the ratio of the volumes of the spherical segment of the liquid phase on the surface of the support and the sphere of the same radius and depends on the wetting angle. A similar relation is valid also for the formation of crystalline nuclei.

It has been shown[34] that a force which tends to increase the radius of curvature acts along the perimeter of the drop wetting the surface of the support. When account is taken of this phenomenon, calculation of the work of formation of the critical nucleus and of its size yield values 1–2 orders of magnitude higher than those obtained when the changes in only volume and surface energy of the nucleus are considered. Whilst remaining within the framework of the macroscopic thermodynamic theory of the heterogeneous formation of a new phase, it is therefore necessary to take into account the linear tension. Neglect of the linear tension may be the reason why, for example, in the electrolytic formation of a new phase on an extraneous electrode, the calculated sizes of the nuclei are found to be of the order of several molecules or even fractions of a molecule. It is of interest to note that in these and other respects experiment agrees with the macroscopic theory.[34]

The satisfactory agreement between the classical ideas about the nucleation and experiment under the conditions of high supersaturation, which is frequently observed, it can be explained by the fact that there is an internal equilibrium in the nucleus (i.e. there is no chemical potential gradient). In this case the thermodynamic theory can be applied to the description of the nucleation of extremely small crystals. Here one must remember that the properties of such ultradisperse systems (including the surface energy) are no longer the same as those of the macrophases and the radius of curvature or the size of the cluster in the nucleation equations are obtained as a result of the replacement of the real system, consisting of two phases and the surface layer between them, by two bodies—the cluster and the parent medium with distinct interfaces.[35] The determination of the size of the crystals and of the surface energies from experimental nucleation data at high supersaturations therefore yields certain idealised values of the process parameters (we shall assume that the terms "nucleus" and "cluster" are equivalent; we have in mind an aggregate of a new phase consisting of a certain number of atoms or molecules).

On the other hand, numerous investigations of the properties of ultradisperse systems have shown[36,37] that for many metals a number of properties of the macrophase persist down to extremely small dimensions.

The main thermodynamic and kinetic characteristics of phase formation in electrochemical systems were first examined about 50 years ago.[38,39] The specific features of electrochemical nucleations have also been discussed in a number of studies.[1,2,6,40,41] The significant characteristics of electrochemical systems are as follows:[40]

(1) The presence of an electrical double layer (EDL) and an electric charge on the species (ions) arriving on the surface of the electrode and hence the need to take into acount the kinetics of charge transfer;

(2) the adsorption of water molecules, cations, anions, and organic substances on the electrode, which leads to a change in the work of formation of the nuclei and in the kinetics of the discharge of the ions;

(3) there is also a possibility of the presence of layers of partly or completely reduced atoms of the metal deposited (adatoms) formed at potentials more positive than the equilibrium value.[42,43]

We shall consider an ideal system which consists of an inert electrode immersed in the electrolyte (the term "inert" implies the absence of interaction between the deposited metal and the support). At equilibrium the electrode has a potential E_0 and the electrochemical potential of the system $\bar{\mu}_0$ is then defined by the expression[44]

$$\bar{\mu}_0 = \mu_p + zF\psi_0 \ ,$$

where μ is the chemical potential of the ion in solution, ψ_0 the Galvani potential at the metal–solution interface corresponding to E_0 (for simplicity, we shall assume that the external potential is zero), z the ionic charge, and F the Faraday.

When the electrode is polarised by an electric current, a potential E is established at the electrode and the Galvani potential and the electrochemical potential of the system change:

$$\bar{\mu} = \mu_p + zF\psi \ .$$

The quantity

$$\Delta\bar{\mu} = \bar{\mu} - \bar{\mu}_0 = zF(\psi - \psi_0) = zF(E - E_0) = zF\eta \tag{4}$$

characterises the deviation of the system from equilibrium, i.e. the degree of supersaturation in the system.[45] Eqn.(4) is valid if the chemical potential of the solution does not change when a current flows. Such conditions obtain for an insignificant change in the bulk-phase concentration of the electrolyte and are characteristic of the initial stages of the electrocrystallisation of metals.

The metal nucleus has a potential equal to the electrode potential E and its formation requires the performance of work proportional to the difference between the electrochemical potentials:[1,2,6,40,41,46]

$$\Delta G = \Phi \frac{16\pi\sigma^3V^2}{3(zF\eta)^2} = \frac{1}{2} n_{cr} zF\eta. \tag{5}$$

The Gibbs–Thomson equation can be written analogously for electrochemical systems:[46]

$$r_{cr} = \frac{2\sigma V}{zF\eta} \ . \tag{6}$$

However, there exist other points of view on the nature of the supersaturation in the electrocrystallisation of metals. For example, it has been assumed[11–13,23,24,47] that the energy relations of the nucleation process are determined by the excess number of the adatoms of the deposited metal on the electrode surface and not by the difference between the electrochemical potentials. It has been postulated[11–13] that the concentration of the adatoms depends only on the potential of the cathode:

$$c_{ad} = c_0 \cdot \exp\left(\frac{zF}{RT}\eta\right) , \tag{7}$$

where c_0 is the concentration of the adatoms at the equilibrium potential and in other studies the need to subtract from the overall overpotential η the overpotential of the transition η_t in order to differentiate the crystallisation overpotential η_c has been noted:[23,24,47]

$$\eta_c = \eta - \eta_t = \frac{RT}{zF} \ln \frac{c_{ad}}{c_0}$$

The work of formation of the nucleus is to be determined from the relation

$$\Delta G = \Phi \frac{16\pi\sigma^3V^2}{3(zF\eta_c)^2} \ .$$

This approach corresponds to the idea of the independence of the stages involving the discharge of ions with formation of adatoms and the actual process involving the formation of nuclei from the discharged atom present on the surface of the support, which in fact denies the possibility of the formation of its nucleus via the direct incorporation mechanism, which is believed by many workers[10,48] to be the most probable for electrochemical nucleation processes. Furthermore, it has been demonstrated[49] for the formation of copper nuclei on pyrographite from a sulphuric acid electrolyte that the concentration of the adatoms affects only the pre-exponential factor in the rate equation and the work of nucleation is determined by the overpotential of the cathode η.

In the atomistic theory[50,51] the supersaturation is also assumed to be $\Delta\bar{\mu} = zF\eta$ and the work of formation of the critical nucleus is calculated from the formula

$$\Delta G = n_{\text{cr}}\Delta\bar{\mu} + \varphi(n_{\text{cr}}),$$

where the function $\phi(n_{\text{cr}})$ characterises the difference between the energy of an n_{cr}-atomic complex and the overall energy of n_{cr} atoms forming part of an infinite crystal:

$$\varphi(n_{\text{cr}}) = n_{\text{cr}}\varphi_{1/2} - \sum_{n=1}^{n_{\text{cr}}} \varphi_n \ , \qquad (8)$$

where $\phi_{1/2}$ is the work required to separate an atom from the "half-crystal" position and ϕ_n is the work of separating an atom from an n-atomic cluster. In terms of its physical significance, $\phi(n_{\text{cr}})$ is equivalent to the surface energy of a complex consisting of n_{cr} atoms.

In contrast to the classical approach, in the given instance the work of formation of the nucleus is not a continuous function of n and the equivalence of the three definitions of the critical nucleus given before therefore breaks down. In the atomistic theory the nucleus is assumed to be critical if its formation requires the expenditure of maximum work. The specific size of the nucleus depends on the structure of the complexes and the interaction forces between the atoms and the support.

The relations between the work of formation of the nucleus, its critical size, and the rate of nucleation have been analysed.[52] Regardless of the approach to the phase formation processes employed, it is possible to formulate the following expressions:

$$\Delta G(n, \Delta\mu) = -n\,\Delta\mu + F(n, \Delta\mu) \ , \qquad (9)$$

$$J = A(\Delta\mu) \cdot \exp\left[-\frac{\Delta G(n_{\text{cr}}, \Delta\mu)}{RT}\right] , \qquad (10)$$

where the number of atoms in the nucleus n is a function of the degree of supersaturation, $F(n, \Delta\mu)$ is the change in the surface energy of the system on formation of an n-atomic complex, and $A(\Delta\mu)$ is the kinetic factor in the equation for the rate of nucleation J. It follows from Eqn.(9) that

$$\left[\frac{\mathrm{d}\,\Delta G}{\mathrm{d}\,\Delta\mu}\right]_{n=n_{\text{cr}}} = -n_{\text{cr}} + \left[\frac{\mathrm{d}\,F(n, \Delta\mu)}{\mathrm{d}\,\Delta\mu}\right]_{n=n_{\text{cr}}} .$$

After taking logarithms and differentiating Eqn.(10) with respect to $\Delta\mu$ at a constant temperature, the following expression was obtained:

$$n_{\text{cr}} = RT\frac{\mathrm{d}\ln J}{\mathrm{d}\,\Delta\mu} - RT\frac{\mathrm{d}\ln A}{\mathrm{d}\,\Delta\mu} + \left[\frac{\mathrm{d}\,F(n, \Delta\mu)}{\mathrm{d}\,\Delta\mu}\right]_{n=n_{\text{cr}}} .$$

When the nucleation processes are considered within narrow ranges of the degree of supersaturation, the changes in the surface energy and the kinetic factor can be neglected:

$$n_{\text{cr}} = RT\frac{\mathrm{d}\ln J}{\mathrm{d}\,\Delta\mu} . \qquad (11)$$

This equation makes it possible to determine the size of the critical nucleus from the experimental dependence of the rate of nucleation of the degree of supersaturation regardless of the nucleus formation model employed. According to the analysis[52] of the influence of the pre-exponential factor in Eqn.(10) and the surface energy $F(n, \Delta\mu)$ on the critical size of the nucleus, the error in the determination of n_{cr} by Eqn.(11) does not exceed 1–2 atoms.

Furthermore, the equations presented above permit the experimental estimation of the limits of applicability of the Gibbs–Thomson equation, since, having determined the rate of nucleation of the crystals for different degrees of supersaturation, it is easy to find the dependence of the critical size of the nucleus on $\Delta\mu$.

III. STATIONARY NUCLEATION KINETICS

The dependence of the stationary rate of nucleation J_0 on the work of formation of nuclei has been obtained in a fundamental investigation:[33]

$$J_0 = D_{\text{cr}} \cdot Z(1) \cdot \exp\left(-\frac{\Delta G}{RT}\right) = K_1 \cdot \exp\left(-\frac{K_2}{\eta^2}\right) , \qquad (12)$$

where D_{cr} is the flux of atoms becoming attached to the critical nucleus, $Z(1)$ the concentration of single atoms, and K_1 and K_2 are constants. As a result of fluctuations, a set of clusters of different size is formed in the system and their number obeys the Boltzmann distribution, so that the product

$$Z(1) \cdot \exp\left(-\frac{\Delta G}{RT}\right)$$

determines the number of critical nuclei.

The fluctuation theory was developed further in a number of studies.[6,30,41,53–58] Becker and Doring[53] used the kinetic approach to establish the relation between J_0 and ΔG. They examined the formation of kinetic nuclei as a chain of successive reactions involving addition to the cluster of or abstraction from the latter of single atoms and obtained the following equation for the rate of nucleation:

$$J_0 = K_1\left(\frac{\Delta G}{n_{\text{cr}}^2 RT}\right)^{1/2} \cdot \exp\left(-\frac{\Delta G}{RT}\right) , \qquad (13)$$

where ΔG is defined by Eqn.(2). The multiplier $(\Delta G/n_{\text{cr}}^2 RT)^{1/2}$, frequently called the Zel'dovich non-equilibrium factor,[6] characterises the deviation of the stationary size distribution of clusters from the equilibrium distribution. Analogous expressions have been obtained for J_0 in other studies.[41,54,57]

Several investigations,[6,53,55] also based on the approach of Becker and Doring, have been devoted to the kinetics of the formation of crystalline nuclei. The authors of these investigations expressed the frequencies of addition and abstraction in terms of the bonding energies between the nearest neighbours in the cluster and obtained equations for the rate of nucleation analogous to Eqn.(13).

The mathematical procedure for the solution of nucleation problems has been improved in a number of investigations.[30,56,59] The following equation has been obtained for the rate of nucleus formation:

$$J = -D(n_{\text{cr}}, t) \cdot Z_e(n_{\text{cr}}, t) \cdot \left[\frac{\partial}{\partial n}\left|\frac{Z(n, t)}{Z_e(n, t)}\right|\right]_{n=n_{\text{cr}}} , \qquad (14)$$

where $Z_e(n, t)$ is the equilibrium distribution function of the nuclei with respect to sizes and $Z(n, t)$ the number of n-atomic clusters at time t. In order to find the specific form of the function $Z(n, t)$, it is essential to solve the differential equation

$$\frac{\partial Z(n, t)}{\partial t} = \frac{\partial}{\partial n}\left[D(n, t) \cdot Z_e(n, t) \cdot \frac{\partial}{\partial n}\left|\frac{Z(n, t)}{Z_e(n, t)}\right|\right] , \qquad (15)$$

which is a complex mathematical task. However, in the stationary case, where the function $Z(n, t)$ can be assumed to be independent of time, the solution greatly simplifies. The expression for the stationary rate of nucleation, obtained by Frenkel'[30] and Zel'dovich,[56] resembles Eqn.(13), which makes it possible to describe fairly accurately the nucleus formation process in real systems.

However, for the analysis of experimental data obtained with narrow ranges of variation of the degree of supersaturation, the employment of the simpler expression (12) is frequently justified.

In examining the nucleation processes in heterogeneous systems, it is essential to take into account the change in the rate of nucleation as a result of the change in both the work of formation of the nucleus, in accordance with Eqn.(3), and in the frequencies of addition and abstraction of atoms.

The occurrence of heterogeneous nucleation via the mechanism involving the direct incorporation of atoms or molecules in the nucleus is unlikely in the gas phase,[31] so that the presence of adatoms on the support and their diffusion along the surface assume considerable importance. These factors have been examined in a review[2] and it has been shown that the rate of nucleation is higher the lower the activation energy for surface diffusion and the stronger the interaction of the adatoms on the support.

Numerous investigators dealt with the influence of the state of the support on the kinetics of nucleation from solutions.[2, 60-71] Ickert[60] considered the influence of chemical interactions during adsorption and the role of the real surface in processes involving the crystallisation of a new phase. The concept of nucleus formation on active centres, which are understood to be the sites on the surface of the support having an increased free energy, has been examined.[61-71] Nuclei are formed preferentially on these centres. Crystal lattice defects (dislocations, vacancies, and inclusions of extraneous atoms), mechanically damaged sites on the surface, or defects in the oxide layer, which are as a rule present on the surfaces of all the supports, can play the role of the active centres. The activity of the centres can vary within fairly wide limits on the same electrode, centres with the highest activity "working" initially, but, as the degree of supersaturation increases, the less active centres also begin to participate in the nucleation process. If the influence of shielding zones, arising around the growing nuclei,[72] can be neglected in a specific system, then the distribution function for the centres with respect to activities can be determined from the experimental dependence of the number of nuclei on the degree of supersaturation.[73]

The relations of the classical theory examined above can be applied also to nucleation processes in electrochemical systems if the degree of supersaturation is expressed in terms of the overpotential of the cathode in accordance with Eqn.(4). However, Eqn.(12) describes satisfactorily only experimental data obtained in systems with high exchange currents within fairly narrow ranges of overpotentials of the cathode, where it is possible to neglect the influence of the rate of discharge of the ions on the surface of the support. In this case the data on the rate of nucleation fit on the linear plots of $\ln J_0$ against $1/\eta^2$ or $\ln J_0$ against η, from the slopes of which it is possible to determine K_2 in Eqn.(12) or the number of atoms in the critical nucleus.

The description of nucleus formation within wide ranges of overpotentials in systems where the charge transfer stage is important requires allowance for the rate of discharge of the ions. A series of studies have been devoted to this problem.[23,24,46,50,51,74-79] It has been suggested[75] that the current density associated with the attachment of atoms to the critical nucleus, growing via the direct incorporation mechanism, be expressed in terms of the cathodic component of the current i_c:

$$i_c = i_0 \cdot \exp\left(\alpha \frac{zF}{RT} \eta\right)$$

and the following equation has been obtained for the stationery rate of nucleation:

$$J_0 = K_1 \cdot \exp\left(\alpha \frac{zF}{RT} \eta\right) \cdot \exp\left(-\frac{K_2}{\eta^2}\right),$$

where α is the electrochemical transfer coefficient and i_0 the exchange current density.

The discharge kinetics have been taken into account analogously in the derivation of equations for J_0 in the region of high overpotentials of the cathode in studies by Milchev and co-workers[50,51] and Chebotin et al.[76] However, this approach is not always justified. The nuclei of the new phase have a considerable surface curvature which affects the kinetics of the discharge of ions on their surface. Equations have been obtained[77] for slow discharge on a curved surface, but the Gibbs–Thomson effect[46] has been taken into account only for the anodic process. A more detailed examination of the kinetics of the discharge of ions on a curved surface has shown that the curvature influences the activation energies for the cathodic and anodic processes.[74,79,80]

The kinetics of the discharge of ions on the curved surfaces of clusters have been taken into account by Danilov and Polukarov.[79] The derivation of equations for the stationary rate of nucleation was based on the kinetic method of Becker and Doring.[53] In the derivation of the expression for the atom addition and abstraction flux densities, the cathodic and anodic components of the current density respectively were employed:

$$i_c = i_0 \cdot \exp\left(\alpha \frac{zF}{RT} \eta\right) \cdot \exp\left(-\alpha \frac{2\sigma V}{rRT}\right),$$

$$i_a = i_0 \cdot \exp\left[-(1-\alpha) \frac{zF}{RT} \eta\right] \cdot \exp\left[(1-\alpha) \frac{2\sigma V}{rRT}\right].$$

The following expressions have been obtained for the rate of nucleation via the mechanism involving the direct incorporation of atoms and nuclei:[79]

$$J_0 = K_1 \left(\frac{\Delta G}{n_{cr}^2 RT}\right)^{1/2} \cdot \exp\left[(1+\alpha) \frac{zF}{RT} \eta\right] \exp\left(-\frac{\Delta G}{RT}\right). \tag{16}$$

The work of formation of the nucleus can be expressed in different ways depending on which nucleation parameter has to be determined. For the estimation of the specific surface energy of the nucleus, ΔG is expressed in accordance with the first part of Eqn.(5) and Eqn.(16) is written in the form

$$J_0 = K_1 \eta^2 \cdot \exp\left[(1+\alpha) \frac{zF}{RT} \eta\right] \cdot \exp\left(-\frac{K_2}{\eta^2}\right). \tag{17}$$

The constant K_2 is determined from the slope of the experimental plot of the rate of nucleation against the overpotential in terms of the variables $\ln \{J_0 \eta^{-2} \exp[-(1+\alpha)zF/RT\eta]\}$ and $1/\eta^2$ and then σ is calculated.[79]

In order to calculate the number of atoms in the critical nucleus n_{cr}, it is necessary to use the second part of Eqn.(5). Eqn.(16) is then transformed into

$$J_0 = K_1 \eta^2 \cdot \exp\left[\left(1 + \alpha - \frac{n_{cr}}{2}\right) \frac{zF}{RT} \eta\right]$$

and n_{cr} can be determined from the formula

$$n_{cr} = \frac{RT}{zF} \left(\frac{d \ln J_0}{d \eta} - \frac{2}{\eta}\right) - 1 - \alpha.$$

Expressions have also been published[79] for the stationary rate of two-dimensional nucleation and nucleus formation via the surface diffusion mechanism.

Models not using macroscopic physical quantities have been proposed for the description of nucleation processes in the range of high degrees of supersaturation.[50,51,76,81–83] The atomistic theory of electrochemical nucleation has been developed by Milchev and co-workers.[50,51] The following expression has been obtained for the direct incorporation mechanism:

$$J_0 = K_1(n_{\mathrm{cr}})\cdot Z_0\cdot\exp[-\varphi(n_{\mathrm{cr}})/RT]\cdot\exp\left[(n_{\mathrm{cr}}+\alpha)\frac{zF}{RT}\eta\right],$$

where $K_1(n_{\mathrm{cr}})$ is a parameter which depends only slightly on the overpotential of the cathode, the function $\phi(n_{\mathrm{cr}})$ is defined by Eqn.(8), and Z_0 is the number of active centres on the support. To a first approximation, the dependence of the surface energy on η is neglected and the equation

$$J_0 = K_1Z_0\cdot\exp\left[(n_{\mathrm{cr}}+\alpha)\frac{zF}{RT}\eta\right] \tag{18}$$

is used.

The expression

$$J_0 = K_1Z_0^2\cdot\exp\left[(n_{\mathrm{cr}}+1)\frac{zF}{RT}\eta\right]$$

has been obtained for the formation of a nucleus via the mechanism involving the surface diffusion of adatoms.[50]

It has been shown[50,51] that the classical and atomistic models of nucleus formation are limiting cases of a single theory and are valid under the conditions of low and high supersaturations respectively. According to the atomistic theory, the number of atoms in the critical nucleus can be arbitrarily small and can even be zero. In this case the critical nucleus is an active centre of the support and addition of one atom to such a centre converts the complex into a stable formation capable of growing spontaneously under the conditions of the given supersaturation. Within the limits of a certain range of values of η, the number of atoms in the nucleus remains constant and then changes abruptly, so that the dependence of the logarithm of the rate of nucleation $\ln J_0$ on the overpotential η should be represented by broken lines. The slope of each section yields n_{cr} and the critical sizes of the nucleus in the neighbouring ranges need not necessarily differ by unity.[45,84]

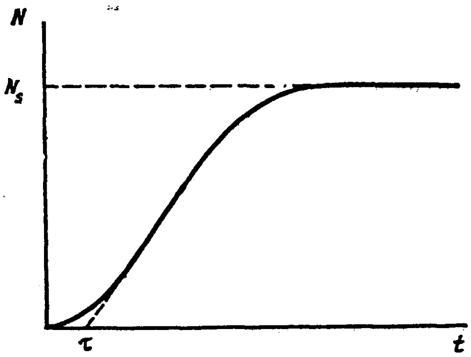
Nucleus formation in the presence on the support of centres with different activities has been examined.[76] Using the main principles of the atomistic theory, the authors obtained the following expression for the stationary rate of nucleation on active centres of the kth kind:

$$J_k = K_k\cdot\exp\left[(m_k+\alpha)\frac{zF}{RT}\eta\right]\cdot\left[1+a_k\exp\left(\frac{zF}{RT}\eta\right)\right]^{-1} \tag{19}$$

where K_k is a constant independent of η in the given range of overpotentials, $a_k = [Z_k(1)/Z_0, k)]_{\eta=0}$, and m_k is the number of atoms in the critical nucleus on the active centres of the kth kind. The numerator of Eqn.(19) yields a linear relation between $\ln J_k$ and η, analogous to that described by Milchev and co-workers,[50,51] while the denominator produces a deviation from it, which may be significant at high overpotentials and for a high adsorption capacity of the support when a_k is fairly large. In the general case, at a given overpotential, there is a set of values of m_k and the overall stationary rate of nucleus formation is determined by the sum of expressions of type (19) with respect to different kinds of active centres.[76]

Extensive experimental data have now accumulated and can be used to test the theoretical calculations for stationary nucleation in electrochemical systems. We shall not dwell on the results obtained within narrow ranges of overpotentials, because they have been examined in detail in a series of reviews.[1,2,4–6,8,9] We shall only mention that their analysis on the basis of the thermodynamic and atomistic models leads to practically identical conclusions and calculations yield similar values of the critical size and of the work of formation of the nuclei.

The determination of data for nucleation kinetics within wide ranges of overpotential is associated with considerable experimental difficulties. The main method of securing information about nucleus formation processes is the determination of the dependence of the number of nuclei of the metal deposited N on the duration of the potential static pulse t (see Figure). The use of the two-pulse method[6,85] enables the nuclei formed during the first pulse to grow further until the attainment of sizes visible under the microscope and makes it possible to count them. The stationary rate of nucleation is determined from the slope of the linear part of the $N(t)$ curve and the thermodynamic process parameters are then evaluated.



Schematic illustration of the dependence of the number of nuclei on the duration of the potentiostatic pulse (τ is the induction period and N_s the limiting number of nuclei).

Valuable results concerning the formation of silver nuclei on vitreous carbon have been obtained.[45,84] The plot of $\ln J_0$ against $1/\eta^2$ exhibits appreciable deviations from linearity, which indicates the inapplicability of Eqn.(12) to the description of the process. Treatment of the results in accordance with the atomistic model showed[45,84] that this theory describes the experiment satisfactorily and makes it possible to estimate the overpotential ranges in which the critical size of the nucleus remains constant: $n_{\mathrm{cr}} = 4$ for $\eta = 25–51$ mV, $n_{\mathrm{cr}} = 1$ for $\eta = 51–160$ mV, and $n_{\mathrm{cr}} = 0$ for $\eta > 160$ mV. However, the results[45,84] can be interpreted also on the basis of the thermodynamic theory.[79] In terms of the variables of Eqn.(17), the experimental data fit satisfactorily on a straight line, from the slope of which it is possible to calculate the constant K_2 and the critical size of the nucleus.

IV. NON-STATIONARY NUCLEUS FORMATION

The stationary course of nucleation can obtain only during a time interval before and after which nucleus formation proceeds under the conditions of a variable rate of nucleation. The increase in the rate of nucleation J in the initial stages of the process is usually attributed to the fact that supersaturation in the system is established not instantaneously but involves the slow formation of a stationary distribution of clusters with respect to size, the accumulation of the adatoms of the deposited metal, and the time variation of the activity of the extraneous electrode. The decrease in the rate of nucleation which follows the stationary section is due to the exhaustion of the active centres of the support, the overlap of the shielding zones, or the coalescence of the growing crystals, which leads to the termination of the nucleation process.

We shall consider the early stages of nucleus formation. Under the conditions of a constant supersaturation, the nucleation process can be described by the Frenkel'–Zel'dovich equations (14) and (15),[30,56] the most accurate solution of which has been obtained[86] on the assumption that the concentration of the adatoms instantaneously assumes the value corresponding to the given supersaturation [see Eqn.(7)]:

$$J(t)=J_0\left[1+2\sum_{m=1}^{\infty}(-1)^m\cdot\exp\left(-m^2\frac{t}{\tau}\right)\right], \tag{20}$$

where

$$J_0=D_{\rm cr}\left(\frac{K}{\pi}\right)^{1/2}Z(1)\cdot\exp\left(-\frac{\Delta G}{RT}\right), \tag{21}$$

$$\tau=4/\pi^2D_{\rm cr}K \tag{22}$$

Here m are positive integral numbers, τ is the induction period, and K is defined by the expression

$$K=-\frac{1}{2RT}\left[\frac{{\rm d}^2\Delta G(n)}{{\rm d}n^2}\right]_{n=n_{\rm cr}}.$$

According to this theory, the main reason for the non-stationary conditions in the early stages of the process is assumed to be the finite rate of establishment of the stationary size distribution of the clusters.

Solutions of Eqn.(15) have been obtained[87,88] taking into account the time-dependent concentration of adatoms using different mathematical approaches. The expression

$$J(t)=\frac{2J_0}{\tau}\sum_{m=1}^{\infty}(-1)^{m+1}m^2\int_0^t c(x)\cdot\exp\left[-\frac{m^2(t-x)}{\tau}\right]{\rm d}x, \tag{23}$$

where J_0 and τ are defined by Eqns.(21) and (22), c is the concentration of adatoms varying with time, and x an auxiliary variable, has been obtained.[88]

The equation for the rate of nucleation obtained by Roldugin et al.[87] is

$$J(t)=\frac{J_0}{c_\eta}\left\{c(t)-\exp\left(-\frac{t}{\tau_1}\right)\left[c_0+\int_0^t\frac{{\rm d}c(x)}{{\rm d}x}\cdot\exp\left(\frac{x}{\tau_1}\right){\rm d}x\right]\right\}, \tag{24}$$

where τ_1 is the induction period due to the redistribution of clusters with respect to size:

$$\tau_1=\frac{1}{4D_{\rm cr}K}=\frac{16RT\sigma}{i_0zF\eta^2}. \tag{25}$$

The second part of Eqn.(25) has been obtained taking into account the Gibbs–Thomson effect, according to which the flux of atoms adding to the critical nucleus in electrochemical systems is equal to the product of the surface area of the critical nucleus and the exchange current density and not the cathodic component of the current. This conclusion arises also from the second definition of the critical nucleus given above. Indeed, the probability of the growth of the nucleus is only equal to the probability of dissolution when the equality

$$i_{\rm c}=i_{\rm a}=i_0,$$

holds. Many investigators failed to take into account this fact in studying the kinetics of electrochemical nucleation.

The time variation of the concentration of adatoms in Eqn.(24) is defined by the expression[89]

$$c(t)=c_\eta-(c_\eta-c_0)\cdot\exp\left(-\frac{t}{\tau_2}\right),$$

where

$$\tau_2=\frac{zFc_0}{i_0^{\rm ad}}\cdot\exp\left[(1-\alpha)\frac{zF}{RT}\eta\right] \tag{26}$$

is the induction period due to the finite rate of accumulation of adatoms, c_η and c_0 are the limiting (for the given overpotential) and equilibrium concentrations of adatoms [see Eqn.(7)], and $i_0^{\rm ad}$ is the exchange current density of the adatoms. Evidently τ_1 diminishes and τ_2 increases with increase in the overpotential of the cathode.[87]

Estimation of the duration of the period of non-stationary conditions from Eqns.(25) and (26) yields times of the order of several milliseconds, which is close to the values determined experimentally, while neglect of the Gibbs–Thomson effect in the derivation of Eqn.(25) leads to values which are smaller by 3–5 orders of magnitude than those observed experimentally.

For $\tau_1=\tau_2=\tau$, Eqn.(24) reduces to

$$J(t)=J_0\left[1-\exp\left(-\frac{t}{\tau}\right)-\frac{c_\eta-c_0}{c_\eta}\cdot\frac{t}{\tau}\cdot\exp\left(-\frac{t}{\tau}\right)\right];$$

and if one of the components of the induction period is much greater than the other, we obtain[87]

$$J(t)=J_0\left[1-\exp\left(-\frac{t}{\tau}\right)\right]. \tag{27}$$

At low overpotentials, the effective induction period is determined by the redistribution of clusters with respect to size and decreases with increasing overpotentials in accordance with Eqn.(25); at $\eta\cong 200$ mV the minimum induction period should be observed and in the region of high supersaturations τ increases with increasing η in accordance with Eqn.(26) and the duration of the non-stationary section is determined by the rate of accumulation of adatoms on the surface of the support.[87] These theoretical estimates have been confirmed by experimental data[84] for the nucleation of silver on vitreous carbons: the relation $\tau(\eta)$ passes through a minimum at overpotentials of ~200 mV.

The influence of the time-dependent supersaturation $\Delta\mu(t)$ on the nucleation kinetics has been analysed by Kashchiev within the framework of the quasi-stationary approximation in two studies[90,91] and the following equations have been obtained:

$$\begin{aligned}J(t)&=J_0(t)\left[1-\frac{\pi^2}{6}n_{\rm cr}(t)\cdot\tau(t)\cdot\frac{{\rm d}\Delta\mu(t)}{{\rm d}t}\right],\\ J_0(t)&=D_{\rm cr}(t)\cdot[K(t)]^{1/2}Z_e[n_{\rm cr}(t),t],\\ \tau(t)&=4/\pi^2D_{\rm cr}(t)\cdot K(t),\\ K(t)&=-\frac{1}{2RT}\left[\frac{{\rm d}^2\Delta G(n,t)}{{\rm d}n^2}\right]_{n=n_{\rm cr}(t)}.\end{aligned} \tag{28}$$

These are valid subject to the condition

$$\frac{{\rm d}\Delta\mu}{{\rm d}t}<\frac{6}{\pi^2n_{\rm cr}(t)\tau(t)}.$$

Eqns.(20), (23), (24), and (28) were obtained for homogeneous nucleus formation but, by introducing the shape factor into the expression for the work of formation of the nucleus in accordance with Eqn.(3), it is possible to use them for the description of heterogeneous processes.[92]

Aleksandrov and Kedyarov[93] took into account the possibility of nucleation in which several energy barriers are overcome at a constant supersaturation and analysed the influence of the multistage course of the process on the nucleation kinetics. In particular, they showed that, in the presence of two energy barriers, the extrapolated induction period can be negative.

Milchev[94,95] developed a theory of non-stationary nucleation based on the assumption that the active centres of the support can arise during the operation of the initiating pulse at a rate which depends on the degree of supersaturation. Since the rate of nucleation is proportional to the number of centres active at the given instant, the stationary state is established only after an induction period during which all the active centres which can arise for the given degree of supersaturation are produced. For electrochemical systems, the active centres are, in particular, defects in the oxide layer on the metallic electrode, which exist before the application of the overpotential pulse or which arise during evaporation. The kinetics of the non-stationary nucleation are described by an equation identical in form to Eqn.(27), but the induction period τ should diminish with increase in the overpotential.

Theories of non-stationary nucleation have been tested thoroughly in a number of studies.[95-102] The integral form of Eqns.(20) and (27) in terms of their dimensionless variables $F = (J_0\tau)^{-1} \int\limits_0^\infty J(t)\mathrm{d}t$ and $y = t/\tau$ is more convenient for comparison with experimental data:

$$F(y) = y - \frac{\pi^2}{6} + 2\sum_{m=1}^{\infty} (-1)^m m^{-2} \cdot \exp(-m^2 y) \,, \qquad (29)$$

$$F(y) = y - 1 + \exp(-y) \,. \qquad (30)$$

It has been established that Eqn.(29) describes satisfactorily the non-stationary nucleation of mercury,[96-99] silver,[100] and cadmium[97,101] on platinum and of copper on pyrographite,[102] but systematic deviations of experimental data from the theoretical curve are observed in the region of low values of the ratio t/τ. Statistical analysis[95] of the experimental data for the nucleation of mercury on platinum showed that a more accurate description of this process is possible on the basis of the theory taking into account the variation of the number of active centres of the support[94] and the corresponding equation (30).

However, one should note that the same experimental data fit fairly well on the theoretical curves corresponding to Eqns.(29) and (30),[87] because the theoretical relations themselves differ insignificantly. The deviations from them are comparable to the experimental errors and the determination of the nature of the non-stationary conditions (the redistribution of the clusters with respect to size, slow accumulation of adatoms, the manifestation of active centres of the support, etc.) therefore requires additional information. It may be that, for each specific system, the non-stationary conditions in the initial stages of the nucleation process are due to specific causes: the state and nature of the support, the experimental conditions, etc.

In the late stages of nucleation, the rate of the process diminishes from J_0 (if it has been attained) to zero. The causes of this phenomenon have been analysed[72,103-106] on the basis of the concept that the aggregates of the new phase are initiated on the active centres of the support.

The phenomenon of such saturation in the formation of mercury nuclei on platinum has been explained[106] by the energetic homogeneity of the surface of the cathode. The possibility of explaining this finding from the standpoint of the concept of the development and overlap of shielding zones arising around the growing nuclei has been demonstrated.[72,103] These models have been generalised in a study[104] according to which the rate of nucleation is given by the relation

$$J(t) = \frac{\mathrm{d}N(t)}{\mathrm{d}t} = J_0\frac{Z_0(t)}{Z_0(0)} = J_0\frac{S(t)}{S(0)} \,,$$

where $Z_0(t)$ is the number of unoccupied active centres and $S(t)$ the surface area of the support not covered by shielding zones. At $t \to \infty$ we have $Z_0(t) \to 0$ and $S(t) \to 0$, which leads to the cessation of the nucleation process. Depending on the experimental conditions, either the exhaustion of the active centres or the overlap of the shielding zone play the decisive role.

The first case is described by the equation

$$N(t) = N_s\{1 - \exp[-J_0(t-\tau)/N_s]\} \,,$$

where $N_S = Z_0(0)$. When the shielding zones play the decisive role, the following expression has been obtained:

$$N(t) = N_s\gamma\left\{\Gamma\left(\frac{2q+2}{2q+1}\right)\frac{J_0(t-\tau)}{N_s}\right\} \,,$$

where Γ and γ are the complete and incomplete gamma-functions.

The quantities $N(t)$, N_S, J_0, and τ are determined directly from experimental plots of the number of nuclei against the duration of the pulse (see Figure) and the parameter q is found from the slope of the plot of $\ln N_S$ against $\ln J_0$.[104] In terms of the dimensionless variables $N(t)/N_S$ and $J_0(t-\tau)/N_S$, it is possible to determine the mechanism of the saturation process. For example, it has been established that, during the formation of mercury nuclei on platinum[105-107] and of copper nuclei on pyrographite,[102] the main role is played by the process involving the overlap of the shielding zones, while in the presence of surfactants the saturation during the nucleation of copper is caused by the exhaustion of the active centres of the support.[102]

V. STATISTICAL ANALYSIS OF NUCLEATION PROCESSES

One of the methods for the experimental study of nucleation kinetics involves the measurement of the time and probability of the appearance of the first nucleus. A random fluctuation process obeys the Poisson law and the probability of the appearance of at least one nucleus is given by[108]

$$P_{\geqslant 1} = 1 - \exp[-N(t)] \,,$$

where $N(t)$ is the average number of nuclei formed at a given overpotential during time t. If there is no induction period, then $N(t) = J_0 t$ and the average expectation time for the nucleus, which can be readily determined experimentally, is given by the formula

$$\bar{t}_1 = \int\limits_0^\infty t\,\mathrm{d}P_{\geqslant 1}(t) = \frac{1}{J_0} \,.$$

The stationary rate of nucleation J_0 can be determined analogously from the probability of the formation of m nuclei:

$$P_{\geqslant m+1} = 1 - \exp(-J_0 t) \cdot \sum_{k=0}^{m} (J_0 t)^k/m! \,,$$

$$\bar{t}_{m+1} = \int\limits_0^\infty t\,\mathrm{d}P_{\geqslant m+1}(t) = \frac{m+1}{J_0} \,.$$

However, in this case it is necessary to demonstrate that the process involving the appearance of m nuclei is random and obeys the Poisson law; this is not always true. For example it has been shown[45,65] that, in the nucleation of silver on vitreous carbon, deviations are observed from the Poisson law for the distribution of distances between nearest nuclei, due to the mutual influence of the growing crystallites.

If the stationary state is attained after an induction period τ, then the probability $P_{\geq 1}$ is given by the expression

$$P_{\geq 1} = 1 - \exp\left[-\int_0^t J(t)\,dt\right] .$$

Knowing the theoretical relation

$$J(t) = J_0 F(t, \tau) ,$$

where $F(t, \tau)$ is a function of time and τ, it is possible to estimate the stationary rates of nucleation and the induction period from the coordinates of the point of inflection P_i and t_i on the experimental plots of the probability of the appearance of the nucleus against time for a constant overpotential. The period τ is calculated from the relation

$$P_i = 1 - \exp\left\{-\left[\int_0^{t_i} F(t, \tau)\,dt\right] \cdot F^{-2}(t_i, \tau)\left[\frac{dF(t, \tau)}{dt}\right]_{t=t_i}\right\}$$

and then the stationary rate of nucleation is evaluated[108] from the formula

$$J_0 = -\ln(1 - P_i)/\int_0^{t_i} F(t, \tau)\,dt$$

A somewhat different mathematical procedure for the determination of J_0 and τ has been used by Milchev and Tsakova.[95] The product $J_0\tau$ is calculated from the formula

$$J_0\tau = \left[\frac{d^2F(y)}{dy^2}\right]_{y=y_i} \cdot \left[\frac{dF(y)}{dy}\right]^{-2}_{y=y_i} , \tag{31}$$

where $F(y) = N(t)/J_0\tau$ and $y = t/\tau$. The ordinate of the point of inflection in the $P_{\geq 1}(t)$ relation is given by the expression

$$P_i = 1 - \exp\left\{-\left[\frac{d^2F(y)}{dy^2}\right]_{y=y_i} \cdot \left[\frac{dF(y)}{dy}\right]^{-2}_{y=y_i} \cdot F(y_i)\right\} ,$$

on the basis of which the calibration curve $P_i(y)$ is plotted, provided that the theoretical relation $F(y)$ is known. Next the values of P_i and t_i are determined from the experimental relation between the probability of the formation of the nucleus and the duration of the potential static pulse and then $y_i = t_i/\tau$ is found with the aid of the calibration curve, the induction period τ is calculated, and the stationary rate of nucleation is evaluated from Eqn.(31).[95]

The theoretical relations (29) and (30) have been tested experimentally[95,101,108] for the nucleation of mercury and cadmium on platinum; satisfactory agreement has been found between the values of J_0 and τ determined from the experimental $N(t)$ relations and the values calculated from the results of statistical analysis.

Fairly numerous studies have been carried out recently on the statistical analysis of the processes involving the formation and growth of nuclei.[1,2,10,109–115] but their detailed examination would require too much space. We shall only note that the methods developed for the calculation of the spatial and temporal distribution of the nucleation steps permit a deeper understanding of the mechanism of nucleus formation and the analysis of the nature of the active centres of the support and of their influences on the kinetics and thermodynamics of nucleation.

VI. THE INFLUENCE OF SURFACTANTS ON THE FORMATION AND GROWTH OF NUCLEI

Surfactants have been used widely and for a long time in the cathodic deposition of metals and alloys to control the physicomechanical and structural properties of galvanic deposits. The theoretical and experimental studies of the influence of surfactants on various stages of electrochemical processes have been thoroughly described in a series of reviews and monographs,[116–119] but their action on phase formation processes has been studied to a much lesser extent.[2,24,73,107,120–125]

It has been shown[120,121] that the adsorption of surfactants in the system can alter the work of formation of nuclei and their critical size by altering the surface energy at the nucleus/electrolyte and nucleus/support interfaces (which is accompanied by a change in the wetting angle and the shape factor).

The influence of saponin on the nucleation of mercury on platinum has been studied[122] and it has been shown that, with increase in the concentration of the additive in solution, the stationary rate of nucleus formation and the number of nuclei N_s in the region of saturation on the $N-t$ curve decrease (see Figure), but the work of nucleation remains almost unchanged under these conditions. According to electrocapillary measurements, no appreciable adsorption of saponin on mercury was observed in the experimental range of potentials and concentrations of the additive, and the authors therefore explain the decrease of J_0 and N_s in terms of the blocking of the active centres of the support. It was suggested that the same centres are active in relation to both adsorption and phase formation processes. Other workers,[107] investigating the mechanism of the influence of poly(propylene glycol) on the nucleation of mercury on platinum, arrived at analogous conclusions.

The influence of acrylamide (AA) and acrylonitrile (AN) on the galvanostatic initiation of the zinc crystals on pyrographite has been investigated.[26,27] Calculation[27] showed that AN increases significantly ΔG as a consequence of its strong adsorption on the surface of the support and, after the introduction into the electrolyte of a combined additive comprising a mixture of AN and AA, the work of nucleation remains almost unchanged compared with the pure zinc sulphate solution. This finding was explained by the simultaneous adsorption of the surfactant on the nuclei and the support, which cancels out the changes in ΔG. However, these calculations, based on the separation of the crystallisation and transition overpotentials, are open to doubt because in the same study it is concluded that the size of the critical nucleus decreases after the adsorption of AN, which is inconsistent with the observed increase of ΔG.

The study of the influence of polyacrylamide (PAA) and acrylic acid (AAC) on the electrocrystallisation of copper under potentiostatic conditions[73,125] showed that PAA is adsorbed only on nuclei of specific size and is not adsorbed on the support, which leads to an increase of N_s, while the initial sections of the $N(t)$ curves in the presence of PAA coincide for the given overpotential. This effect has been explained by the decreased rate of growth of the shielding zone arising around the growing crystallites. In contrast to PAA, AAC is adsorbed on the pyrographite support and eliminates active centres, which decreases J_0 and N_s and also increases the period of non-stationary conditions.

Thus the majority of investigators have concluded that the influence of surfactants on the initial stages of electrocrystallisation is manifested mainly by the inversion of the ratio of the rates of formation and growth of the nuclei of the new phase as a result of the blocking of the active centres of the support and the inhibition of the discharge of ions on the surfaces of the growing crystallites.

VII. MODELS OF NUCLEATION TAKING INTO ACCOUNT THE GROWTH OF NUCLEI

The study of the character of the growth of nuclei can yield important information about the nucleation processes.[1,2] Analysis of the potentiostatic current–time relations (transients) has been recently used increasingly to determine the phase formation relations. The theory governing the growth of two-dimensional layers[10,127–139] and three-dimensional crystals has been confirmed by experimental studies of electrocrystallisation on dislocation-free phases of silver single crystals[10,140–146] and the formation of anodic films[147–154] and metallic nuclei,[155–159] and by mathematical modelling.[139,160–165] Investigators have devoted much attention to the role of processes involving mass transfer to the growing nuclei.[166–173]

In the present review we shall confine ourselves to the analysis of the most important studies of the three-dimensional nucleus formation and growth, which occur widely in processes involving the deposition of galvanic coatings on supports made of a different material. A general model taking into account the two-dimensional initiation and subsequent three-dimensional growth of crystals has been proposed.[174–177]

The relations governing the growth of nuclei were analysed for the first time by Sheludko and Bliznakov,[126] who derived the relation between the current associated with the growth of a single semispherical nucleus I_1 and time t for different rate-limiting stages. Under the conditions of slow discharge of ions, the current is proportional to t^2, while in processes subject to diffusional and ohmic control it is proportional to $t^{1/2}$, but the character of the dependence of the current on the potential differs significantly, which permits the experimental differentiation of the above growth mechanisms.

In the further development of the theory, the growth of an ensemble of nuclei was examined. For the diffusional growth regions, satisfactory results were provided by the model based on local semispherical diffusion;[178] corrections have been applied[17,80,179] for the initial radius of the nucleus and the Gibbs–Thomson effect. The experimental $I(t)$ relations were interpreted on the assumption of the independent increase of N for the crystallites, i.e. it was assumed that the overall current is equal to the sum of the individual currents associated with the growth of the nuclei. The following expression is then obtained for the instantaneous nucleation (the formation of N nuclei at a rate greatly exceeding the rate of their growth):

$$I_N(t) = NI_1(t),$$

while for progressive nucleation (when the rate of nucleus formation and growth are comparable)

$$I_N(t) = J_1Z_0I_1(t)\cdot t,$$

where J_1 is the specific (referred to one active centre) rate of nucleation and $I_1(t)$ the current associated with the growth of a single nucleus. An experimental test showed[17,80,178–184] that, despite the satisfactory agreement between experiment and theory in the description of the growth of single nuclei, we have $NI_1(t) > I_N(t)$ even in the initial stages of the process, which indicates a significant mutual influence of the growing nuclei.

Scharifker and Hills[185] took into account the overlap of the semispherical diffusion zones arising around the growing crystallites and obtained the following expression for the current associated with the growth of N nuclei formed simultaneously:

$$I_N(t) = zFc_v\left(\frac{D}{\pi t}\right)^{1/2}\cdot[1-\exp(\pi NkDt)], \tag{32}$$

where c_v is the volume concentration of the electrolyte, D the diffusion coefficient, and k the rate constant for the growth of the zone:

$$k = (8\pi c_v V)^{1/2}.$$

For progressive nucleation, the current is described by the expression

$$I_N(t) = zFc_v\left(\frac{D}{\pi t}\right)^{1/2}\cdot\left[1-\exp\left(-\frac{2}{3}\pi J_1Z_0kDt^2\right)\right]. \tag{33}$$

The plots of the growth current, corresponding to Eqns.(32) and (33), pass through a maximum, whose coordinate I_m and t_m can be readily found from the condition that the derivatives of the current with respect to time are zero. The product

$$I_m^2t_m = \delta D(zFc_v)^2,$$

where δ is a numerical multiplier equal to 0.1629 for instantaneous nucleation and 0.2598 for progressive nucleation, does not contain the quantities N and J_1Z_0 and is therefore a diagnostic criterion of the initial mechanism.[185] Furthermore, instantaneous and progressive nucleation can be distinguished on the basis of the experimental $I(t)$ relations plotted in terms of the variables $(I/I_m)^2$ and t/t_m and one can then calculate the quantities N and J_1Z_0. If the initiation ceases as a result of the overlap of the diffusion zones, then the limiting number of nuclei is given by the expression

$$N_s = \left(\frac{3J_1Z_0}{8kD}\right)^{1/2}.$$

Comparison of the relations obtained with the experimental data for the nucleation of lead on zinc oxide and of copper sulphide on copper[185] demonstrated a satisfactory agreement between theory and experiment.

The theory was developed further by Scharifker and Mostany.[186] In their study of diffusion-controlled nucleation on a limited number of active centres of the support, the authors of the above investigation were able to derive a system of transcendental equations, whose solution permits the independent calculation of J_1 and Z_0 from the experimental coordinates of the maximum on the current transient. Yet another advantage of this theory is the possibility of describing a diffusion-controlled potentiostatic initiation and growth process in a general form, where the instantaneous and progressive nucleation are limiting special cases.

Analysis of the current transients for the lead nucleation process on structureless carbon[187] demonstrated that the number of active centres on which the nuclei are formed increases with increasing overpotential but is almost independent of the electrolyte concentration. Furthermore, the concentration dependence of the rate of nucleation permits the conclusion that the atoms are directly incorporated in the nucleus without the intermediate deposition of adatoms. Treatment of the experimental data in accordance with the classical and atomistic nucleation theories leads to virtually identical critical sizes of the nucleus ($n_{cr} < 1$).

An interesting approach in the analysis of the formation and growth of nuclei was employed by Isaev and Baraboshkin.[188] Equations permitting the description of the nucleation processes under the conditions of diffusional and kinetic control of growth were derived on the basis of Kolmogorov's theory.
If the instantaneous nucleation takes place under the conditions of slow discharge of ions, then the current is defined by the expression

$$I = 2i_g x_1 \omega(x_1),$$

where

$$i_g = i_0 \cdot \exp\left(\alpha \frac{zF}{RT}\eta\right) - i_0 \cdot \exp\left[-(1-\alpha)\frac{zF}{RT}\eta\right]$$

and $\omega(x_1)$ is the tabulated Dawson integral:

$$\omega(x_1) = \exp(-x_1^2) \cdot \int_0^{x_1} \exp(x^2)\,dx ,$$

and the variable x_1 is defined by the expression

$$x_1 = i_g V (\pi N)^{1/2} t / zF .$$

The $I(x_1)$ relation has a maximum at $x_1 = 1.50$, which corresponds to the product $x_1\omega(x_1) = 0.64$ and the degree of surface coverage of the electrode by the growing deposit $\theta = 0.90$.

For diffusional control of growth, x_2 is described by the expression

$$x_2^2 = 2Dc_v V \cdot \pi N t \left[1 - \exp\left(-\frac{zF}{RT}\eta\right)\right]$$

and the following equation is valid for the current:

$$I = 2zFDc_v (\pi N)^{1/2} \cdot \omega(x_2) \left[1 - \exp\left(-\frac{zF}{RT}\eta\right)\right].$$

When $x_2 = 0.92$, a current maximum corresponding to $\omega(x_2) = 0.54$ and $\theta = 0.57$ is observed.

For progressive nucleus formation with kinetic control, the following equation has been obtained:

$$I = 3i_g \omega_2(x_3) ,$$

where

$$\omega_2(x_3) = \exp(-x_3^3) \cdot \int_0^{x_3} (x_3^2 - x^2) \cdot \exp(3x_3x^2 - 2x^3)\,dx ,$$

$$x_3^3 = \frac{i_g^2 V^2 \pi J_0}{3(zF)^2} t^3$$

Here the quantities $x_3 = 1.34$, $\omega_2(x_3) = 0.44$, and $\theta = 0.91$ correspond to the current maximum.

If the rate of the process is limited by bulk diffusion, then the following relation holds:

$$I = zF \left\{4Dc_v \left[1 - \exp\left(-\frac{zF}{RT}\eta\right)\right]^{3/4}\right\} \cdot \left(\frac{\pi J_0}{V}\right)^{1/4} \omega_4(x_4) ,$$

where

$$\omega_4(x_4) = \exp(-x_4^4) \cdot \int_0^{x_4} (x_4^2 - x^2) \cdot \exp(2x_4^2x^2 - x^4)\,dx ,$$

$$x_4^4 = Dc_v V \pi J_0 \left[1 - \exp\left(-\frac{zF}{RT}\eta\right)\right] \cdot t^2 .$$

In this case $x_4 = 1.08$, $\omega_4(x_4) = 0.36$, and $\theta = 0.4$ correspond to the current maximum.

The equations obtained make it possible to infer the mechanism of nucleation (instantaneous or progressive), to deduce the factor controlling the growth of nuclei (slow discharge of ions or volume diffusion), and to calculate the degree of coverage of the electrode by the deposit and the parameters of the initiation process.

The method of current transients has been used[189–193] to investigate the influence of the degree of surface coverage of the electrode by adatoms on the kinetics of three-dimensional nucleation. At potentials more positive than the equilibrium potential for the deposition of lead on the (111) and (100) faces of silver single crystals, a certain definite number of adatoms were deposited, an overpotential pulse was applied, and the time variation of the current was measured. The transients were treated on the assumption that the nucleation is progressive with diffusional control of the growth of semispherical nuclei in accordance with the theory developed in a number of investigations[180–183,194–196] and the rate of initiation of lead crystals was calculated. It was shown that, with increase in the degree of surface coverage by the adatoms, the rate of nucleation diminishes and does not increase as should have been expected.

This non-trivial fact was explained as follows: previously it had been established that the structures of the sorption layer of the adatoms and of the bulk phase of the metal differ appreciably from one another.[189,190,192] The formation of a three-dimensional nucleus therefore requires a rearrangement of the adsorption layer, whose rate depends on the density, symmetry, and ideality of the two-dimensional film. The dependence of the rate of nucleation on the potential at which the adsorption layer was formed on the surface can also be associated with the decrease of the number of active centres of the support as a result of the two-dimensional association of the adatoms or the adsorption of microimpurities.

According to the calculation based on the atomistic model of nucleation, the critical nucleus consists of 11 and 13 atoms for overpotentials in the range 10–20 mV on the (111) and (100) faces of silver single crystals respectively. Since the rate of initiation on the (100) face is much higher than on the (111) plane and the work of formation of nuclei is approximately the same, one may conclude that the preliminary maintenance of the electrode at potentials more positive than the equilibrium value influences mainly the kinetic factor in Eqn.(18) for the rate of nucleation.[193] It is therefore quite evident that, in the study of nucleus formation on supports made of a different material, it is necessary to take into account the possibility of the formation of adsorption layers or two-dimensional nuclei even in the anodic range of potentials.

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The data considered in the review show that during recent years there has been a significant expansion of the range of studies on the initial stages in electrocrystallisation. New trends have arisen in research, in particular, a more logical allowance has been made for the specific features of the electrochemical reactions in the crystal initiation processes, a method has been developed for the analysis of the time variation of the current whereby one can estimate the number of nuclei generated and infer the mechanism of their growth, which splendidly supplements the classical two-pulse method. Interesting results have been obtained in the study of the dependence of the rate of initiation of crystal formation on the degree of coverage by adsorption layers made up of atoms of the metal deposited in the range of potentials more positive than the equilibrium potential of the phase. Systematic research has been begun on the influence of surfactants in the stage involving the initiation and growth of crystals.

The model ideas in the studies described are based on the assumption the absence of interaction between the nuclei formed. However, under the conditions of high supersaturation, which usually obtain in the electrodeposition of metals, the processes involving the coalescence of the nuclei with formation of aggregates are apparently entirely probable. There is no doubt that further study of the influence of surfactants and of the multistage occurrence of electrochemical reactions on nucleation processes will yield useful data both for the theory of electrochemical phase formation and for the practical deposition of galvanic coatings.

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Spectral Sensitisation of Photoprocesses in Polymeric Donor-Acceptor Systems

A.V.Vannikov and A.D.Grishina

Processes are considered which involve the spectral sensitisation of polymeric electron donor-electron acceptor (EDA) systems as a result of which an electron is transferred and charged species are formed under the influence of visible light. Problems of the practical utilisation of the phenomenon in the development of light-sensitive recording layers, photovoltaic cells transforming light into electrical energy, and polymeric photoconductors are discussed.
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I. INTRODUCTION

The sensitisation of electron transfer reactions in EDA complexes to radiation at specific wavelengths, particularly in the visible spectral range, has been studied in detail as a fundamental problem of the effect of electromagnetic radiation on organic systems and also in connection with the possible practical applications of this phenomenon. This concerns the employment of organic complexes as photoconductors, as light-sensitive recording layers, and in photovoltaic cells transforming solar energy into electrical energy. The sensitisation is important also in the photochemical oxidation of organic compounds and in the utilisation of solar energy by photochemical methods.

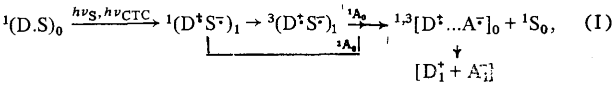
In the present review the concept of "polymeric electron donor—electron acceptor (EDA) complexes" includes not only complexes formed by polymeric components but also complexes which contain low-molecular-weight compounds distributed in a polymer matrix.

Questions concerning the spectral sensitisation of polymer compositions, incorporating donors (D), acceptors (A), and also weak charge-transfer complexes (CTC or D.A) are examined below. The sensitisation is achieved by introducing an additional component—the sensitiser (S), which exhibits optical absorption in the specified wavelength range. The present review does not discuss processes described in detail in existing publications[1-3] and based on the ionic dissociation reaction of polymer CTC ($D.A \xrightarrow{h\nu_{CTC}} D^{+\cdot} + A^{-\cdot}$) as a result of direct photoexcitation. We shall consider reactions involving sensitised electron transfer and reactions due to the sensitised formation of singlet oxygen.

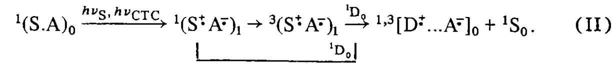
1. The Principal Types of Sensitised Charge-Transfer Reactions

(a) Reactions with Participation of the Sensitiser in Electron Transfer

The sensitiser forms CTC with the donor or acceptor component:



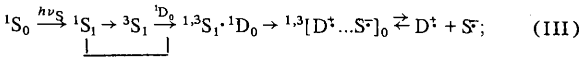
$$ {}^1(D.S)_0 \xrightarrow{h\nu_S,\,h\nu_{CTC}} {}^1(D^{+\cdot}S^{-\cdot})_1 \rightarrow {}^3(D^{+\cdot}S^{-\cdot})_1 \xrightarrow{{}^1A_0} \underset{\displaystyle \downarrow \atop \displaystyle [D_1^+ + A_1^-]}{{}^{1,3}[D^{+\cdot}\ldots A^{-\cdot}]_0} + {}^1S_0, \qquad (I)$$



$$ {}^1(S.A)_0 \xrightarrow{h\nu_S,\,h\nu_{CTC}} {}^1(S^{+\cdot}A^{-\cdot})_1 \rightarrow {}^3(S^{+\cdot}A^{-\cdot})_1 \xrightarrow{{}^1D_0} {}^{1,3}[D^{+\cdot}\ldots A^{-\cdot}]_0 + {}^1S_0. \qquad (II)$$

Here ${}^{1,3}(D^{+\cdot}S^{-\cdot})_0$ and ${}^{1,3}(S^{+\cdot}A^{-\cdot})_1$ are the singlet- or triplet-excited complexes and ${}^{1,3}[D^{+\cdot}\ldots A^{-\cdot}]_0$ is a geminal radical-ion pair in a singlet or triplet state.

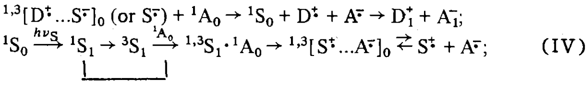
The sensitiser forms a collision complex with the donor or acceptor component and also with the complex ${}^1(D.A)_0$:



$$ {}^1S_0 \xrightarrow{h\nu_S} {}^1S_1 \rightarrow {}^3S_1 \xrightarrow{{}^1D_0} {}^{1,3}S_1\cdot{}^1D_0 \rightarrow {}^{1,3}[D^{+\cdot}\ldots S^{-\cdot}]_0 \rightleftarrows D^{+\cdot} + S^{-\cdot}; \qquad (III)$$

secondary reaction:

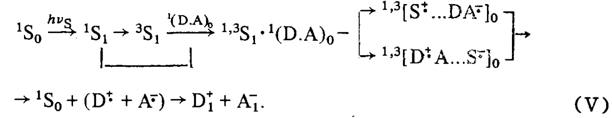
$$ {}^{1,3}[D^{+\cdot}\ldots S^{-\cdot}]_0 \,(\text{or } S^{-\cdot}) + {}^1A_0 \rightarrow {}^1S_0 + D^{+\cdot} + A^{-\cdot} \rightarrow D_1^+ + A_1^-;$$



$$ {}^1S_0 \xrightarrow{h\nu_S} {}^1S_1 \rightarrow {}^3S_1 \xrightarrow{{}^1A_0} {}^{1,3}S_1\cdot{}^1A_0 \rightarrow {}^{1,3}[S^{+\cdot}\ldots A^{-\cdot}]_0 \rightleftarrows S^{+\cdot} + A^{-\cdot}; \qquad (IV)$$

secondary reaction:

$$ {}^{1,3}[S^{+\cdot}\ldots A^{-\cdot}]_0 \,(\text{or } S^{+\cdot}) + {}^1D_0 \rightarrow {}^1S_0 + D^{+\cdot} + A^{-\cdot} \rightarrow D_1^+ + A_1^-;$$

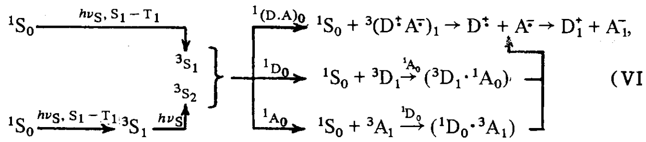


$$ {}^1S_0 \xrightarrow{h\nu_S} {}^1S_1 \rightarrow {}^3S_1 \xrightarrow{{}^1(D.A)_0} {}^{1,3}S_1\cdot{}^1(D.A)_0 - \left[\begin{array}{l} \rightarrow {}^{1,3}[S^{+\cdot}\ldots DA^{-\cdot}]_0 \\ \rightarrow {}^{1,3}[D^{+\cdot}A\ldots S^{-\cdot}]_0 \end{array}\right] \rightarrow$$

$$ \rightarrow {}^1S_0 + (D^{+\cdot} + A^{-\cdot}) \rightarrow D_1^+ + A_1^-. \qquad (V)$$

${}^{1,3}S_1.{}^1D_0$, ${}^{1,3}S_1.{}^1A_0$, and ${}^{1,3}S_1.{}^1(D.A)_0$ are collision complexes.

(b) The Sensitiser Subjected to One-Quantum or Two-Quantum Excitation is the Donor of Triplet Energy



(VI)

Processes (I)—(VI) have come to be referred to as autosensitisation when $S \equiv D_1^+$ or A_1^-.

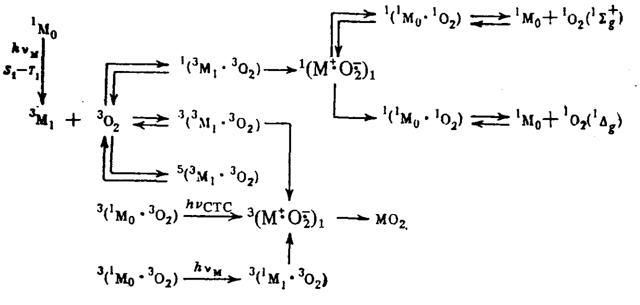
(c) Reactions with Participation of Singlet Oxygen

In the presence of O_2, singlet molecular oxygen is formed in the reaction with the triplet-excited organic molecule (${}^3M_1$) (${}^1O_2$ can be in the ${}^1\Sigma_g^+$ and ${}^1\Delta_g$ states). The reactions involving ${}^1O_2$ are used in information recording processes.

The quantum yield of $^1O_2$ is determined by the relative positions of the $E(^3M_1)$ level and the level of the excited charge-transfer state $E[^{1,3}(M^{\dot{+}}O_2^{\dot{-}})_1]$.

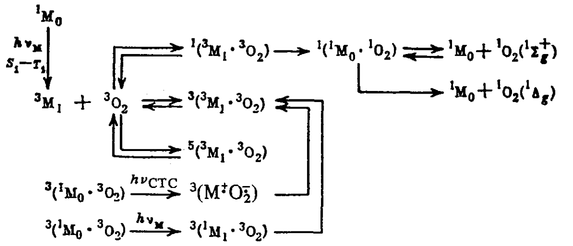
When the $E[^{1,3}(M^{\dot{+}}O_2^{\dot{-}})_1]$ level lies below $E(^3M_1)$, singlet oxygen is formed via the following reactions:

Scheme 1



When the $E[^{1,3}(M^{\dot{+}}O_2^{\dot{-}})_1]$ level lies above $E(^3M_1)$,[4,5] the direct involvement of the $^{1,3}(M^{\dot{+}}O_2^{\dot{-}})_1$ states in the process is ruled out:

Scheme 2



Comparison of the reactions via Schemes 1 and 2 shows that in the latter case only one pathway leads to the decomposition of the collision complex $^3M_1.^3O_2$ via the singlet state $^1(^3M_1.^3O_2)$ with formation of singlet oxygen, while in the former case, other conditions being equal, the reaction involving the decomposition via the state $^3(M^{\dot{+}}O_2^{\dot{-}})_1$, which does not lead to $^1O_2$, is included. Taking into account the ratios of the populations of levels with different multiplicities, one can postulate that the quantum yield in the formation of singlet oxygen via Scheme 2 will exceed by a factor of 4 the quantum yield in the formation reaction via Scheme 1.

II. PROBLEMS OF THE PRACTICAL UTILISATION OF SENSITISED ELECTRON PHOTOTRANSFER IN EDA COMPLEXES

In the development of recording polymeric donor–acceptor systems for photovoltaic cells sensitive to a given wavelength range, the sensitisers employed are dyes of different classes (cyanine, thiazine, xanthene, etc., dyes), variable valence ions, porphyrins, which are used in silver halide photography[6,7] and in the creation of liquid-phase photochemical systems transforming the energy of solar radiation into electrical or chemical energy.[8-11]

The reduction of acceptors [viologens (V^{2+})] sensitised by ruthenium complexes [including tris(2,2′-bipyridyl)ruthenium(II) or $Ru(bipy)_3^{2+}$], porphyrins, and dyes in the presence of donors of different nature has been successfully investigated in recent years in connection with the search for new systems for the storage of solar energy.[8-12] At the same time, in order to create non-silver (or low-silver) information recording systems, studies have been made of the reduction of acceptors (viologens) in the donor matrix of poly(vinyl alcohol) (PVA) under the conditions of the phoeoexcitation of additionally introduced sensitisers: riboflavin[13,14] and benzophenone.[15] For this purpose, we can also employ a system comprising V^{2+} and $Ru(bipy)_3^{2+}$ incorporated in a cellophane matrix.[12] A high sensitivity has been obtained in the composition deposited on a triacetate support and comprising PVA as the donor, *NN′*-bis(p-cyanophenyl)-4,4′-bipyridyl chloride as the acceptor, and riboflavin as the sensitiser. Excitation of riboflavin by light with $\lambda \cong 360-440$ nm in the PVA donor matrix ensures electron transfer from the matrix to the sensitiser with formation of the reduced form of riboflavin—a semiquinone radical, with a quantum yield of 0.09.[16] In the presence of V^{2+} the subsequent dark electron transfer from this radical to viologen ensures the formation of latent image centres—the radical-cations $V^{\dot{+}}$, for the visualisation and enhancement of which a physical development process is employed[14] with formation of a visible image made up of metallic silver:

$$B^{\dot{+}} + Ag^+ \rightarrow B^{2+} + Ag^0;\ Ag^0 + nAg^+ + nFe^{II} \rightarrow Ag^0Ag_n + nFe^{III}$$

The sensitivity $S_{0,1}$ to monochromatic light with $\nu_{inc} = 436$ nm was determined as the reciprocal of the exposure $H_{0,1}$ (in J cm^{-1}) for which the optical density on the exposed sections exceeds after development by 0.1 the optical density on the unexposed sections (the fog density):[14]

$$S_{0,1} = 1/H_{0,1} = 6.62\cdot 10^3\ \mathrm{cm^2\ J^{-1}}$$

Attempts have been made to create liquid-phase photogalvanic cells based on the photochemical reduction of thiazine dyes in the presence of iron(II).[17,18] Different versions of the recording of the effect of light, consisting in the photochemical reduction of thiazine dyes in the presence of donors of different nature and subsequent electron transfer from the reduced form of the dye to the metal cations in solid matrices, have been described by Oster.[19]

The products of the photochemical reduction of thiazine dyes—semiquinone radicals—initiate the polymerisation of vinyl and acrylic monomers.[19-22] A system based on the polymerisation of acrylic monomers initiated by the radical-cations $MbH^{\dot{+}}$ (Mb^+ is the dye Methylene Blue) has been used for the phase recording of holograms.[23] The effective photochemical reduction of Mb^+ was ensured by the presence in the reaction mixture of a donor—toluenesulphonic acid. The holograms were recorded by means of laser radiation with $\lambda = 632.8$ nm, which induces the photoexcitation of the dye Mb^+. It has been established[23] that two mechanisms are responsible for the phase recording: the first involves the formation of the relief and the second involves a change in the refractive index of the medium as a result of polymerisation. 4-Nitrophenylacetic acid was introduced into the reaction mixture to fix the light-sensitive layer. The dye Mb^+ decomposes irreversibly under the conditions of the photoexcitation of the acid by UV radiation. A light sensitivity of ~10^3 cm^2 J^{-1}, a resolution of 1500 mm^{-1}, and a diffraction efficiency of ~45% were attained: the contribution by the change of the refractive index is ~12% and the modulation of the thickness is ~33%.

Gelatine layers containing *N*-vinylcarbazole (VCA and CBr_4, distributed in the matrix in the form of particles whose size ranges from 0.5 to 20 μm, exhibit a high light sensitivity, approaching that of silver halide emulsions ($S_{0,2} = 3 \times 10^6$ cm^2 J^{-1} for the negative process and 3×10^4 cm^2 J^{-1} for the positive process).[24] Depending on the order in which photoexcitation and heat treatment are applied, a positive or negative process is achieved. Under the conditions of the photoexcitation of the sensitiser—the VCA.CBr_4 CTC, the latter undergoes ionic dissociation with formation of the active products $VC^{\dot{+}}$ and $Br^-...\dot{C}Br_3$, which initiate the polymerisation of VCA whose high concentration is due to its disperse state. A high quantum yield of the polymer is achieved by the subsequent intensification of the image by the alternate heat treatment of the entire layer and its exposure to intense illumination.

Sensitised donor–acceptor systems based on diazonium salts [p-aminobenzenediazonium sulphate and salts having the general formula $p\text{-X–C}_6\text{H}_4\text{–}\overset{+}{\text{N}}\equiv\text{N BF}_4^-$, where X = $(\text{C}_2\text{H}_5)_2\text{N}$, CH_3O, Br, CH_3COO, or NO_2] as acceptors[16,25–33] have been proposed for the recording of information. The donors employed are toluenesulphonic acid, sodium toluene-p-sulphonate, diphenylamine, 1,4-diazobicyclo[2.2.2]octane,[25–28] hypophosphorous acid, ascorbic acid, and the polymeric PVA matrix [combined with poly(ethylene glycol) as plasticiser].[16,29–33]

The sensitisers are dyes (thiazine, acridine, and xanthene dyes), riboflavin,[16,25–33] and variable-valence ions.[33] The essential components are also phenols and an acid stabiliser. In these systems the recording of information is due to the decomposition of the acceptors (diazonium salts) as a result of electron transfer, initially from the donor to the photoexcited sensitiser and then from the reduced sensitiser to the acceptor.

The image appears on treatment of the exposed layer with ammonia, which transforms the phenol $\text{RC}_6\text{H}_4\text{OH}$ into phenoxide ions ($\text{RC}_6\text{H}_4\text{O}^-$). The latter, which have more pronounced electron-donating properties than $\text{RC}_6\text{H}_4\text{OH}$, enter into the dark azo-coupling reaction with the acceptor preserved in the unexposed sections—the diazonium salts. This leads to the formation of the azo-dye and the colouring of the unexposed sections:

$$\text{ArN}_2^+ + \text{RC}_6\text{H}_4\text{O}^- \rightarrow \text{Ar—N=N—RC}_6\text{H}_3\text{OH}$$

The products of the photochemical decomposition of the diazonium salts do not react with phenoxide ions.

Depending on the polarity of the medium, the diazonium salts decompose via either ionic (heterolytic decomposition in polar matrices) or radical (homolytic decomposition in non-polar matrices) mechanisms:

$$p\text{-X—C}_6\text{H}_4\text{—N}_2^+ + \text{e} \rightarrow p\text{-X—C}_6\text{H}_4^{\cdot} + \text{N}_2$$

As a result of the interaction of the aryl radicals formed in the homolytic decomposition with H-donors (RH), new electron-donating free radicals R$^\bullet$, inducing the additional decomposition of the diazonium salt, are formed.[16,27] The formation of free radicals is used to initiate the polymerisation of the acrylamide introduced additionally into the layer.[28] The photoexcitation of Mb^+ by light with $\lambda = 665$ nm in a system containing p-aminobenzenediazonium sulphate as the acceptor, sodium toluene-p-sulphonate as the donor, Mb^+ as the sensitiser, and also acrylamide results in the formation of polyacrylamide (molecular weight $M = 7 \times 10^6$) with a quantum yield $\phi = 1.3 \times 10^4$. As noted above, the photosensitive dye Mb^+ initiates the polymerisation of monomeric acrylamide derivatives even in the absence of a diazonium salt. For example, the transformation of acrylamide into the polymer ($M = 9 \times 10^5$) has been found to occur[28] with a quantum yield of 1.7×10^3.

Layers based on polyvinylcarbazole (PVCA) and polyepoxypropylcarbazole (PEPC) as donors with acceptors of different nature, after the additional introduction of sensitising dyes, acquire a photosensitivity over a wide spectral range, including the absorption band of the dye. Rhodamine 6G, coumarin 6,[34] eosin,[35] as well as cyanine dyes with electron-accepting properties,[36] whose ground level lies below the upper limit of the valence band of PVCA are effective spectral sensitisers for PVCA. The effects of the sensitised photoconductivity in these systems have been discussed in detail.[1–3]

It is noteworthy that injection and chemical sensitisations are widely used for PVCA layers. Injection sensitisation at the PVCA/selenium boundary arises when aromatic molecules are introduced and is due to the formation on the interface of CTC between selenium and the aromatic molecule,[37] which equalise the "ceilings" of the valence bands of selenium and PVCA and ensure the transfer to PVCA of the holes† photogenerated in selenium.

Chemical sensitisation is ensured by the introduction of additives such as trichloroacetic acid[38] and diazonium salts[39–43] in a system consisting of a donor (PVCA) and a spectral sensitiser or acceptor (o-dinitrobenzene, trinitrofluorenone). The introduction of such additives increases the photoconductivity of the system almost by an order of magnitude and leads to the appearance of a "memory effect" consisting in an increase by 3–4 orders of magnitude (up to 24 h) of the time during which the photocurrent decreases after the illumination has been switched off. The effects are associated with the interaction of the radical-anions ($\text{A}^{\overline{\cdot}}$ or $\text{S}^{\overline{\cdot}}$), formed in the phototransfer of electrons, with the additive introduced (for example, $\text{A}^{\overline{\cdot}} + \text{H}^{\overset{+}{\cdot}} \rightarrow \text{HA}^{\overline{\cdot}}$), which lowers the rate constants for the bulk-phase recombination of the electron–hole pairs. The "memory effect" is used in the recording of information under electrophotographic conditions. A simplified scheme for the electrophotographic process on PVCA layers consists in the following steps: the layers are negatively charged uniformly with the aid of a corona discharge. After exposure, free holes, recombining with the surface negative charge, are generated in the section of the layer acted upon by light. This results in the formation of potential relief on the surface, which reproduces the distribution of illumination during exposure. The development is carried out with the aid of charged dye species.[1,44,Ch.2] The time required for this process, from exposure to development, is determined by the "retention" time of the charge on the surface, which generally speaking is short (not more than several minutes). The "memory effect" makes it possible to simplify significantly this process and to expose the uncharged surface of the film, i.e. to separate the charging and exposure stages in time and as regards apparatus. The retention of increased electroconductivity on the exposed section permits the visualisation of the image by charging the surface along time after exposure.

In photovoltaic cells and in information recording processes, it is possible to use systems which are a combination of thin metal layers and organic semiconductors. Layers of pure PVCA or PVCA containing disperse ZnO,[45] deposited on a metallic layer, are used for the electrophotographic process. In order to sensitise these systems with respect to visible light, a dye is introduced at the metal/organic layer interface. By employing dyes of different nature (sensitisers for either ZnO or PVCA), it has been established[45] that the primary stage is the photochemical oxidation of the sensitiser dye with electron transfer from the photoexcited dye to ZnO, while the secondary stage is the electron transfer from PVCA to the oxidiser sensitiser. As a result of this process, a pair of charged species is generated, which can recombine or move apart into space, contributing to the photoconductivity of the layer.

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†Here and henceforth we shall speak of p-type (holes) and n-type (electrons) charge carriers in those cases where there is a possibility of the movement of electrons via the $\text{M}\ldots\text{M}^{\dot{+}}\ldots\text{M}$ and $\text{M}\ldots\text{M}^{\overline{\cdot}}\ldots\text{M}$ systems, where M is a neutral molecule and $\text{M}^{\dot{+}}$ and $\text{M}^{\overline{\cdot}}$ are radical-cation and radical-anion respectively.

The use of organic layers in photovoltaic cells for the transformation of solar energy into electrical energy is of special interest. The Schottky barrier, arising in the organic layer when it comes into contact with the metal, is usually employed for this purpose. Since the organic semiconductors usually exhibit p-type conductivity, a necessary condition for the formation of the Schottky barrier is $\Phi_m < \Phi_{sc}$ (Φ_m and Φ_{sc} are the electron work functions for the metal and semiconductor respectively). In this case, the organic metallic layers are charged positively and negatively respectively on contact, the height of the Schottky barrier does not exceed the difference $V_0 = \Phi_{sc} - \Phi_m$, and the electric field in the barrier region is $E_d = 2V_0/d$ (d is the width of the barrier).

The advantages of systems based on the Schottky barrier are the low cost of the necessary components and the ease of divising a technology for the preparation of the cells. Among the numerous studies devoted to this problem, we shall be interested in communications about the preparation of organic layers based on phthalocyanine without a metal (Phtc) dispersed in a polymer matrix.[46-48] Maximum efficiencies for organic systems (several per cent) have been attained on such layers sensitised by dyes. In principle, the mechanism of the generation of charge carriers in these systems is the same as in organic layers with a homogeneous distribution of the dye and semiconductor in the polymer. However, there are also specific features associated with the fact that the dye is distributed at the disperse Phtc/metal interface. In this case the redox processes in the solid-phase system proceed with electron transfer across the interface. Furthermore, for Phtc it is possible to employ the ideas of the band model of solids. Compared with the sputtered Phtc layers, polymer layers with dispersed Phtc particles make it possible to obtain cells with much higher efficiencies.[48] The main element of the photovoltaic cell is a thin (~1 μm) layer of the polymer (PVA, PVCA, polycarbonate) in which the particles of polycrystalline Phtc, with linear dimensions of several hundreds of ångstroms, are linearly distributed. This layer is deposited on a conducting support forming an ohmic contact with the latter (this requires the fulfillment of the condition $\Phi_{sup} > \Phi_{Phtc}$). A transparent layer of SnO_2 on glass or quartz and also metals (Au, Ag, Cu, Pt), are used as the conducting supports. A semitransparent layer of metal with a low electron work function is sputtered onto the free surface of the organic layer. The most stable characteristics of the cells have been obtained with indium ($\Phi_{In} = 4.0$ eV, $\Phi_{Phtc} = 5.1$ eV). When the cell is illuminated from the side of the metallic layer (for the maximum effectiveness, it is important that all the light is absorbed in the region of the barrier), electron–hole pairs are generated, are separated in the field E_d, the electron passes to the metal, and the positive charge passes into the bulk phase of the semiconductor. If the cell is in a closed electric circuit, then a short circuit current I_{sc} arises in the circuit on illumination. When the circuit is broken, a potential difference is generated in the metallic and SnO_2 layers—the open-circuit photo-e.m.f. (V_{oc}) which cannot exceed V_0. When a load resistance R is included in the external circuit, its value determines V and I generated when the cell is illuminated and the useful work is then VI.

The photo-e.m.f. and the photocurrent at which the useful work is a maximum are designated by V_{max} and I_{max}. In order to estimate the efficiency of the cell, the so called filling factor F is introduced:[34]

$$F = \frac{I_{max} V_{max}}{I_{sc} V_0}.$$

I_{sc}, V_0, and F can be calculated from the voltage–current characteristic of the cell on illumination.

The efficiency of the photovoltaic cell can be calculated relative to the intensity of the light incident on the cell L_0:

$$\eta = \frac{I_{sc} V_0 F}{L_0} \cdot 100\% \tag{1}$$

or relative to the intensity of the light which has passed through the metallic electrode L_T:

$$\eta' = \frac{I_{sc} V_0 F}{L_T} \cdot 100\% \tag{2}$$

The efficiency η characterises the efficiency of the cell as a whole and η' characterises the efficiency of the transformation of the energy at the barrier.

The quantum efficiency of the photogeneration of charge carriers can be obtained from I_{sc}:[34]

$$\varphi = 1.24 I_{sc}/L_T \lambda_{inc}, \tag{3}$$

where I_{sc} is expressed in A cm^{-2} and L_T in W cm^{-2}; λ_{inc} (nm) is the wavelength of the incident radiation.

The photocurrent spectrum is correlated with the absorption spectrum of Phtc, which indicates the independence of ϕ of λ_{inc} ($\phi = 0.27$ and $F = 0.33$). For monochromic radiation, $\lambda_{inc} = 670$ nm, $L_T = 6$ μW cm^{-2}, $I_{sc} = 1.4 \times 10^{-6}$ A cm^{-2}, $V_0 = 0.86$ V, $\eta' = 6.5\%$, and $\eta = 2\%$. However, for radiation having the same spectral composition as sunlight, $L_T = 1$ mW cm^{-2} (0.01 of the intensity of solar radiation) and $\eta' = 0.5\%$. With increase of L_T to 10 mW cm^{-2}, η' falls to 0.07%. The most readily understood pathways leading to an increase of η' are associated with the increase of I_{sc} owing to the increase of ϕ and the more effective absorption of sunlight, since the optical absorption by Phtc in the green part of the spectrum, where the maximum energy of solar radiation is concentrated, exhibits a break. The increase of ϕ on excitation by light corresponding to the absorption band Phtc can be achieved as a result of the chemical sensitisation of the system, for example, by introducing an acceptor which forms a CTC with Phtc. By selecting dyes having an absorption maximum in the green gap in the absorption by Phtc, it is possible to achieve the spectral sensitisation of the layer, which should ultimately also lead to an increase of ϕ and I_{sc}. The mechanisms of sensitisation have been discussed in two communications[34,35] and will be described in Section III.

Layers for the recording of information based on CTC between donors [aromatic amines (Am)] and acceptors (carbon tetrabromide (CBr_4) or bis(tribromomethyl) sulphone ($CBr_3SO_2CBr_3$)], which are sensitive to light in the wavelength range below 500 nm, have been sensitised with respect to visible light by the introduction of cyanine dyes;[3, Ch.5; 44, Ch.6; 49,50]. As in the silver halide process, the spectral sensitisation of these non-silver photographic systems is due to electron phototransfer reactions.

Non-silver photographic systems based on CTC between donors of different nature [the leuco-form of Crystal Violet,[51] PVCA,[52] 1,1-bis(*p*-dimethylaminophenyl)ethylene and *p*-diethylaminostyrylquinoline,[53] and benzyldiphenylamine and dibenzylaniline;[3, Ch.5; 44, Ch.6] and acceptors (CBr_4 and CHI_3) exhibit a high light sensitivity ($S_{02} \cong 10^5$ cm^2 J^{-1} [3,13, 51-58]) by virtue of the possibility of the optical intensification of the latent image, first established by Fotland.[51] The possibility of the optical intensification of the latent image is due to the fact that the coloured product formed as a result of the photodissociation of the CTC (in the final form[13,51-53, 55-57] or intermediate form[3, Ch.5; 44, Ch.6; 50,58]) is a sensitiser (autosensitiser) of a CTC-based composition for light in the region of the intrinsic absorption. The idea has been developed[51–53] that the mechanism of the optical intensification is due to the transfer of triplet energy from the photo-excited coloured product to the nearest CTC. A two-quantum mechanism of this process in the system based on the CTC between benzylamines and CBr_4 has been established.[58]

III. REACTIONS WITH PARTICIPATION OF THE SENSITISER IN ELECTRON TRANSFER

1. Energy Relations

In estimating the efficiency of electron transfer, the relative positions of the energy levels of the interacting components are compared. Together with energy characteristics such as the ionisation potential of the molecule I_M (I_D for the donor) or the electron affinity of the molecule E_M (E_A for the acceptor) in the condensed phase one uses the equilibrium oxidation-reduction potentials. The relation between these quantities is given by Eqns.(4) and (4a) for the ionisation potential and (5) and (5a) for the electron affinity

$$I_M^p = I_M^{liq} + (E_M^{\dot{+}} - P_M^{\dot{+}}), \qquad (4)$$

$$I_M^{liq} = I_M^{gas} - E_M^{\dot{+}} = E_0 + eE_{1/2}(M/M^{\dot{+}}), \qquad (4a)$$

$$E_M^p = E_M^{liq} - (E_M^{\dot{-}} - P_M^{\dot{-}}), \qquad (5)$$

$$E_M^{liq} = E_M^{gas} + E_M^{\dot{-}} = E_0 + eE_{1/2}(M^{\dot{-}}/M). \qquad (5a)$$

Here the superscripts p, liq, and gas denote the values of I_M and E_M in the polymer and in the liquids and gas phases respectively, $E_M^{\dot{+}}$ or $E_M^{\dot{-}} = (e^2/2r^{\pm})(1 - 1/\kappa)$ is the change in the real solvation energy in the liquid phase in the transition from the molecule to the radical-cation or radical-anion respectively, κ the dielectric constant of the liquid in which the potentials $E_{1/2}^{ox,\ red}$ have been measured,

$$P_M^{\dot{+}} \text{ or } P_M^{\dot{-}} = \frac{e^2}{2r^{\pm}}\left(1 - \frac{1}{\kappa_p}\right) \qquad (6)$$

the change in the polarisation energy of the polymer in the transition from the molecule to the radical-cation or radical-anion respectively, κ_p the dielectric constant of the polymer layer, $r^{\pm}$ the radius of the radical-cation or radical-anion respectively, $E_{1/2}^{ox} \equiv E_{1/2}(M/M^{\dot{+}})$ the equilibrium potential of the oxidation of the molecule via the redox reaction

$$M \rightleftarrows M^{\dot{+}} + e(S \rightleftarrows S^{\dot{+}} + e,\ D \rightleftarrows D^{\dot{+}} + e), \qquad (VII)$$

$E_{1/2}^{red} \equiv E_{1/2}(M^{\dot{-}}/M)$ the equilibrium potential of its reduction via the redox reaction

$$M^{\dot{-}} \rightleftarrows M + e(S^{\dot{-}} \rightleftarrows S + e,\ A^{\dot{-}} \rightleftarrows A + e), \qquad (VIII)$$

and E_0 the position of the level of the reference electrode relative to which the equilibrium oxidation-reduction potentials $E_{1/2}(M/M^{\dot{+}})$ and $E_{1/2}(M^{\dot{-}}/M)$ measured in the liquid phase are reckoned. According to Gurevich and co-workers,[59–61] $E_0 = \Phi + e\Delta\Phi$—reckoned from the vacuum energy of the electron in the Fermi level of the reference electrode at the equilibrium electrode potential—is determined as the electron work function (for the ejection of the electron into the gas phase) of the material of the reference electrode (Φ) with allowance for $\Delta\Phi$, where $\Delta\Phi$ is the surface potential jump due to the interaction of the reference electrode with the oriented solvent molecule; $\Delta\Phi$ depends on the nature of the reference electrode and the solvent.[59,60] Using $\Phi = 4.5$ eV and $e\Delta\Phi = -0.07$ eV for the platinum reference electrode in 1 *N* aqueous acid solution (normal hydrogen electrode: n.h.e), $E_0 = 4.43$ eV (n.h.e) was obtained.[60,61] This corresponds to $E_0 = 4.67$ eV (saturated calomel reference electrode: sat.c.e) and $E_0 = 4.62$ eV [silver chloride reference electrode in the 1 : 1 (vol.%) methanol: water mixture: Ag/AgCl].[62]

It has been noted[59] that the potential $\Delta\Phi$ is known only for some metal–solution combinations. Apparently for this reason E_0 is frequently identified with Φ. For example, E_0 has been estimated in a review,[8, p.199] as $\Phi = 4.5–4.7$ eV (n.h.e.).

It follows from the analysis of literature data that $\Delta\Phi' = 0.53$ V, i.e. the potential of the reaction at the reference electrode

$$e\ (\text{in Hg}) + HgCl_{surf} \rightleftarrows Hg^0 + Cl^-.$$

and not $E_0 = 5.07$ eV (sat.c.e.),[63,64] obtained on the basis of the idea that $E_0 = \Phi + e\Delta\Phi'$ in which $\Phi = 4.54$ eV was adopted, has been used in investigations in recent years.

The energy E_0 of the saturated calomel electrode has been calculated[65] from the measured redox potentials in aromatic hydrocarbons (AH). E_0 was obtained by adding together Eqns.(4a) and (5a) for the same molecule:

$$E_0 = \frac{I_{AH}^{gas} + E_{AH}^{gas}}{2} - \frac{e[E_{1/2}(AH/AH^{\dot{+}}) + E_{1/2}(AH^{\dot{-}}/AH)]}{2} + (E_{AH}^{\dot{-}} - E_{AH}^{\dot{+}}).$$

According to experimental data, we have

$$(I_{AH}^{gas} + E_{AH}^{gas})/2 = 4.34 \text{ eV};$$

$$\frac{e[E_{1/2}(AH/AH^{\dot{+}}) + E_{1/2}(AH^{\dot{-}}/AH)]}{2} = -0.31 \text{ eV (sat.c.e.)};$$

$$E_{AH}^{\dot{+}} = E_{AH}^{\dot{-}} = 1.94 \text{ eV}.$$

Thus $E_0 = 4.65$ eV (sat.c.e.). According to experimental estimates for aromatic hydrocarbons,[65, 66, 67] arylazonaphthols,[68] and cyanine dyes,[69] $E_M^{\dot{-}} \cong E_M^{\dot{+}} \cong 1.8–2.0$ eV in media with $\kappa > 10$ [when $(1 - 1/\kappa) \cong 1$].

Comparison of the values of I_M^{gas} measured by different methods and $E_{1/2}(M/M^{\dot{+}})$ yielded the relation

$$I_M^{gas} = E_0' + eE_{1/2}(M/M^{\dot{+}}) \qquad (4b)$$

in which $E_0' = E_0 + E_M^{\dot{+}} = 4.65 + 1.94 = 6.59$ eV (sat.c.e.),[65] $E_0' = 6.5$ eV (sat.c.e.),[70, 71] and $E_0' = 4.5 + 1.94 = 6.44$ eV (n.h.e.) [66] have been quoted for aromatic hydrocarbons in acetonitrile and $E_0' = 4.51 + 1.84 = 6.35$ eV (Ag/AgCl) for cyanine dyes in water (pH 10).[69, 72, 73]

Comparison of the values of E_A^{gas} measured by the magnetron method with the equilibrium potentials $E_{1/2}(A^{\dot{-}}/A)$ for strong acceptors (mainly those containing cyano-groups) yielded the relation[74]

$$E_A^{gas} = E_1'' + eE_{1/2}(A^{\dot{-}}/A), \text{ eV}, \qquad (5b)$$

in which $E_0'' = E_0 - E^{\dot{-}} = 2.7$ eV was obtained for solutions in acetonitrile. Similar values of E_0'' have been obtained for cyanine[69] and thiazine[75] dyes. It follows from the comparison of Eqns.(4b) and (5b) that $(E_M^{\dot{+}} + E_M^{\dot{-}}) = (E_0' - E_0'') = 3.89–3.8$ eV for the radical-ions derived from large molecules with conjugated bonds and that the real formation energy is $E_M^{\dot{+}} \cong E_M^{\dot{-}} \cong 1.95–1.9$ eV.

The polarisation energy in the solid medium P_M^{+} or P_M^{-} is determined by comparing I_M^{gas} with the threshold value for photoelectron emission.

The photoelectron emission from organic solids (including polymers) has been analysed in monographs.[76, 77] By comparing I_M^{gas} [78] with the threshold values of the photoelectron emission from compounds of different classes,[77] it is possible to estimate $P_M^{\dot{+}} \cong 1.5–1.9$ eV from Eqns.(4) and (4a). For molecules at an interface, $P_M^{\pm}$ differs from the value characteristic of the molecules within the solid phase.[47, 7] At the interface between phases having the dielectric constants κ_1 and κ_2, the energy $P^{\pm} = (e^2/2r^{\pm})(1 - 1/\kappa')$, where

$\kappa' = (\kappa_1 + \kappa_2)/2$; at the air–solid interface, $\kappa' = (1 + \kappa_{\mathrm{solid}})/2$.[36] For PVCA molecules, the polarisation energy of the radical-cation has been determined as the difference $P^{+\cdot} = I^{\mathrm{gas}}_{\mathrm{PVCA}} - I^{\mathrm{layer}}_{\mathrm{PVCA}} = 1.5$ eV [79] on the assumption that $I^{\mathrm{gas}}_{\mathrm{PVCA}} = I^{\mathrm{gas}}_{\mathrm{IPC}} = 7.6$ eV, where IPC = *N*-isopropylcarbazole. The value $I^{\mathrm{layer}}_{\mathrm{PVCA}} = 6.1$ eV has been obtained[79] by comparing the electron work function for metals *in vacuo* and the threshold energy of the light quanta ensuring the photoemission of holes from metals, sputtered onto a PVCA layer, into this polymer layer. The polarisation energies ~1.2 to 2.04 eV and 1.8 eV for aromatic hydrocarbons in polystyrene and poly(methyl methacrylate) respectively have been published in a monograph.[80] These values represent the differences between the threshold values for two-quantum ionisation of molecules in the gas phase and in the polymer matrix.

Taking into account the scatter of the values of E_0, $E^{\pm}_{\mathrm{M}}$, and $P^{\pm}_{\mathrm{M}}$ quoted in the above study, one can propose the following expressions relating the ionisation potentials of the molecule in the polymer matrix $I^{\mathrm{p}}_{\mathrm{M}}$ and the electron affinity $E^{\mathrm{p}}_{\mathrm{M}}$ to the equilibrium redox potentials.

$$I^{\mathrm{p}}_{\mathrm{M}} = E_0 + 1.9\left(\frac{1}{\kappa_{\mathrm{p}}} - \frac{1}{\varkappa}\right) + \mathrm{e}E_{1/2}(\mathrm{M}/\mathrm{M}^{+\cdot}),\ \mathrm{eV}, \tag{7}$$

$$E^{\mathrm{p}}_{\mathrm{M}} = E_0 - 1.9\left(\frac{1}{\kappa_{\mathrm{p}}} - \frac{1}{\varkappa}\right) + \mathrm{e}E_{1/2}(\mathrm{M}^{-\cdot}/\mathrm{M}),\ \mathrm{eV}, \tag{8}$$

where $E_0 = 4.6$ eV (sat.c.e.), 4.55 eV (Ag/AgCl in 1:1 (vol.%) $CH_3OH:H_2O$ mixture, and 4.36 (n.h.e.). The following notation has been adopted below:

$$\Delta G^{+}_{\mathrm{p}} = \Delta G^{-}_{\mathrm{p}} = 1.9\left(\frac{1}{\kappa_{\mathrm{p}}} - \frac{1}{\varkappa}\right)$$

$$eE'_{1/2}(\mathrm{M}/\mathrm{M}^{+\cdot}) = eE_{1/2}(\mathrm{M}/\mathrm{M}^{+\cdot}) + \Delta G^{+}_{\mathrm{p}},\ eE'_{1/2}(\mathrm{M}^{-\cdot}/\mathrm{M}) = eE_{1/2}(\mathrm{M}^{-\cdot}/\mathrm{M}) - \Delta G^{-\cdot}_{\mathrm{p}}. \tag{9}$$

2. Relative Positions of the Levels in the Electron Phototransfer Process

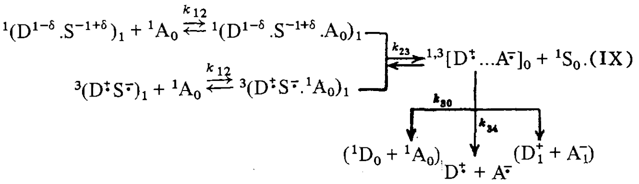
The quantum-mechanical theory of the elementary electron transfer step has been examined in detail in a monograph.[81,82] The relation between the rate constant for the quenching of the photoexcitation of molecules via electron transfer and the free energy of activation for this process in liquid media has been discussed.[83–89] In the present review attention is concentrated on the analysis of the energy characteristics of the components involved in the redox reactions and the relations between them as factors determining the direction and mechanism of the redox processes in these systems. In the development of photochemically active polymeric media on the basis of EDA complexes, the components D and A, forming either weak CTC or contact complexes corresponding to the complete electron transfer from D to A in the excited state, are employed. The use of CTC with a low-lying level and involving complete charge transfer would lead to the dark accumulation of electron transfer products.

We shall consider initially reactions with participation of the complexes D.S or S.A [compounds (I) and (II)]. Under the conditions of the formation of electron donor–electron acceptor complexes between S and D or A, there is a possibility of the processes illustrated in Fig.1. In the case of the CTC $^1(\mathrm{D.S})_0$, these processes can be represented by process (I) (Fig.1*a*):

$$\begin{tikzcd}
{}^1(\mathrm{D}^{+\delta}.\mathrm{S}^{-\delta})_0 \arrow[r, "h\nu_{\mathrm{S}}"] & ({}^1\mathrm{D}_0.{}^1\mathrm{S}_1); \arrow[d] \\
{}^1(\mathrm{D}^{+\delta}.\mathrm{S}^{-\delta})_0 \arrow[r, "h\nu_{\mathrm{CTC}}"] & {}^1(\mathrm{D}^{1-\delta}.\mathrm{S}^{-1+\delta})_1 - {}^3(\mathrm{D}^{+\cdot}\mathrm{S}^{-\cdot})_1.
\end{tikzcd}$$

Here δ is the degree of charge transfer in the ground state of the complex and $^1(\mathrm{D}^{1-\delta}.\mathrm{S}^{-1+\delta})_1$ the lowest excited singlet state of the CTC. For contact complexes, δ = 0 and $^1(\mathrm{D}^{1-\delta}.\mathrm{S}^{-1+\delta})_1 \equiv {}^1(\mathrm{D}^{+\cdot}\mathrm{S}^{-\cdot})_1$.

Next follows the formation of the collision complex with A (with the constant k_{12}) and electron transfer (k_{23}):



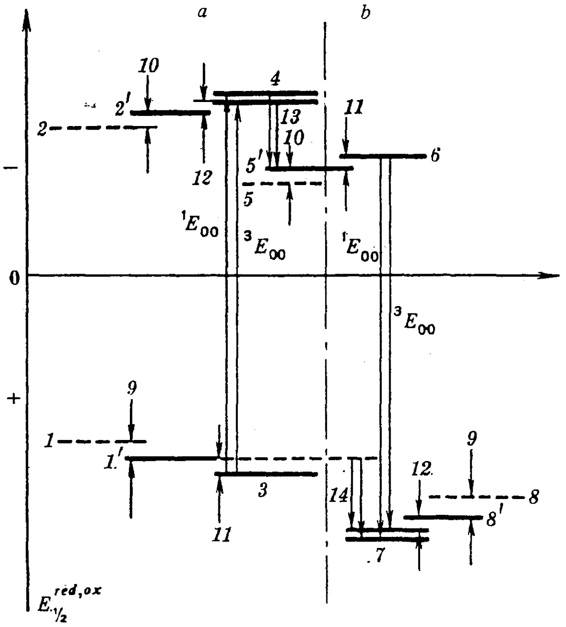


Figure 1. Schematic illustration of the relative positions of the oxidation-reduction potentials of the donor (D), the acceptor (A), and the complexes D.S (*a*) and S.A (*b*) in the ground and excited states; S = sensitiser; continuous line—polymer matrix; dashed line—liquid phase: *1*) and *1'*) $E_{1/2}({}^1\mathrm{D}_0/\mathrm{D}^{+\cdot})$, $E'_{1/2}({}^1\mathrm{D}_0/\mathrm{D}^{+\cdot})$; *2*) and *2'*) $E_{1/2}(\mathrm{S}^{-\cdot}/{}^1\mathrm{S}_0)$, $E'_{1/2}(\mathrm{S}^{-\cdot}/{}^1\mathrm{S}_0)$; *3*) $E_{1/2}[{}^1(\mathrm{D.S})_0/(\mathrm{D}^{+\cdot}\mathrm{S})]$; *4*) $E_{1/2}[{}^{1,3}(\mathrm{D}^{+\cdot}\mathrm{S}^{-\cdot})/.(\mathrm{D}^{+\cdot}\mathrm{S})$; *5*) and *5'*) $E_{1/2}(\mathrm{A}^{-\cdot}/{}^1\mathrm{A}_0)$, $E'_{1/2}(\mathrm{A}^{-\cdot}/{}^1\mathrm{A}_0)$; *6*) $E_{1/2}.[(\mathrm{SA}^{-\cdot})/{}^1(\mathrm{S.A})_0$; *7*) $E_{1/2}[(\mathrm{SA}^{-\cdot})^{1,3}(\mathrm{S}^{+\cdot}\mathrm{A}^{-\cdot})_1]$; *8*) and *8'*) $E_{1/2}.({}^1\mathrm{S}_0/\mathrm{S}^{+\cdot})$, $E'_{1/2}({}^1\mathrm{S}_0/\mathrm{S}^{+\cdot})$; *9*) $\Delta G^{+}_{\mathrm{p}}$; *10*) $\Delta G^{-}_{\mathrm{p}}$; *11*) *X*; *12*) $\Delta G^{\mathrm{p}}_{\mathrm{CTC}}$; *13*) ΔG_{23} (IX); *14*) ΔG_{23} (X).

The free energy ΔG_{23} (IX) of the electron transfer stage of reaction (IX) represents the difference between the redox potentials (Fig.1a):

$$\Delta G_{23}(\mathrm{IX}) = eE'_{1/2}[{}^{1.3}(\mathrm{D}^{+\cdot}\mathrm{S}^{-\cdot})_1/(\mathrm{D}^{+\cdot}\mathrm{S})] - eE'_{1/2}(\mathrm{A}^{-\cdot}/{}^1\mathrm{A}_0) \tag{10}$$

In this formula $E'_{1/2}[{}^{1/3}(\mathrm{D}^{+\cdot}\mathrm{S}^{-\cdot})_1/(\mathrm{D}^{+\cdot}\mathrm{S})]$ is the potential, adjusted to the polymer matrix, for the oxidation of the excited complex in the redox reaction

$$^{1,3}(\mathrm{D}^{+\cdot}\mathrm{S}^{-\cdot})_1 \rightleftarrows (\mathrm{D}^{+\cdot}\mathrm{S}) + \mathrm{e}$$

$$[\text{or } {}^1(\mathrm{D}^{1-\delta}.\mathrm{S}^{-1+\delta})_1 \rightleftarrows (\mathrm{D}^{+\cdot}\mathrm{S}) + \mathrm{e}],$$

which can be calculated from the relation

$$eE'_{1/2}[^{1,3}(D^{+\cdot}S^{-\cdot})_1/(D^{+\cdot}S)] = eE'_{1/2}[^1(D.S)_0/(D^{+\cdot}S)] - {}^{1,3}E_{00}, \qquad (11)$$

where $^{1,3}E_{00}$ is the distance from the ground to the excited singlet or triplet level of the complex:

$$eE'_{1/2}[^1(D.S)_0/(D^{+\cdot}S)] = eE_{1/2}(^1D_0/D^{+\cdot}) + X + \Delta G^+_p \qquad (11a)$$

—the equilibrium potential, adjusted to the polymer matrix, for the oxidation of the complex in the ground state by the reaction

$$^1(D.S)_0 \rightleftarrows (D^{+\cdot}S) + e.$$

In Eqn.(11a), X is the formation energy of the complex; for contact complexes, the term $X = 0$ and for CTC we have

$$X = \frac{\{W_{01} - eS_{01}[E'_{1/2}(^1D_0/D^{+\cdot}) + E_0]\}^2}{e[E'_{1/2}(^1D_0/D^{+\cdot}) - E'_{1/2}(S^{-\cdot}/^1S_0)] + (P^+_D + P^-_S) - (Q^{gas} + P)},$$

where $W_{01} = \int \phi_1(D,S)H\phi_2(\overset{+}{D^{\cdot}}S^{-\cdot})d\tau$ is the energy of the interaction of uncoupled states $[\phi_1(D,S)]$ and states corresponding to the total charge transfer between the components $[\phi_2(D^{+\cdot}S^{-\cdot})]$; $W_{01} = 0$ for contact complexes and $W_{01} \cong 0.05$ to 0.5 eV for CTC; $S_{01} = \int \phi_1(D,S)\phi_2(D^{+\cdot}S^{-\cdot})d\tau$ the overlap integral of the wavefunctions of these states; $S_{01} = 0$ for contact complexes and $S_{01} = 0.01$–0.1 for CTC. $Q^{gas} = e^2/2r$ is the energy of the Coulombic attraction of the radical-ions in the state $^{1,3}(D^{+\cdot}S^{-\cdot})_1$ in the gas phase.

$$P = 2\mu^2\left(\frac{\kappa_p - 1}{2\kappa_p + 1}\right)/a^3 \qquad (12)$$

P is the energy of the polarisation of the polymeric medium by the dipole $^{1,3}(D^{+\cdot}S^{-\cdot})_1$ including the rapid electronic and also the atomic and slow orientational components. $\mu = er_{D^{+\cdot}S^{-\cdot}} \cong 2er$ is the dipole moment, $a(\cong 2r)$ the radius of the cavity of the polarising dipole, and $r = r^+ = r^-$ the radius of the radical-cation or radical-anion. Hence

$$Q^{gas} + P = 1.9\left(\frac{4\kappa_p - 1}{2\kappa_p + 1}\right).$$

In reaction (IX) the lifetime of the polar states $^1(D^{1-\delta}.S^{-1+\delta}.A)_1$ is $>10^{-12}$ s when the formation of the collision complex between the excited complex and the molecule A is a result solely of the increase of the size of the complex on its photoexcitation. During this period, only the electronic polarisation of the medium is established (whence $\kappa_p = n^2$, n being the refractive index). At the same time, under the conditions of the segmental mobility of the polymer unit, collision with a molecule can occur after the relaxation of the excited complex to a state of equilibrium ($^{1,3}E_{00}$) corresponding to the polarisation energy P and hence corresponding to equilibrium in relation to the redox potential of the excited complex:

$$^{1,3}E_{00} = I^{gas}_D - E^{gas}_S + X - (Q^{gas} + P) + {}^{1,3}Q_e = e[E'_{1/2}(^1D_0/D^{+\cdot}) - E'_{1/2}(S^{-\cdot}/^1S_0)] + X + \Delta G^P_{CTC} + {}^{1,3}Q_e, \qquad (13)$$

$$\Delta G^P_{CTC} = (P^+_D + P^-_S) - (Q^{gas} + P), \qquad (14)$$

where $^1Q_e = X + {}^1Q'_e$, $^1Q'_e = J_{12} + K_{12}$, and $^3Q_e = J_{12} - K_{12}$ are the interelectron repulsion energies in the singlet-excited and triplet-excited complex. J_{12} and K_{12} are the Coulombic and exchange energies respectively.[90]

According to Eqns.(11), (11a), and (13),

$$eE'_{1/2}[^{1,3}(D^{+\cdot}S^{-\cdot})_1/(D^{+\cdot}S)] = eE_{1/2}(S^{-\cdot}/^1S_0) - \Delta G^P_{CTC} - \Delta G^-_P - {}^{1,3}Q_e. \qquad (15)$$

Thus we obtain from Eqns.(10) and (15) (Fig.1*a*):

$$\Delta G_{23}(IX) = e[E_{1/2}(S^{-\cdot}/^1S_0) - E_{1/2}(A^{-\cdot}/^1A_0)] - \Delta G^P_{CTC} - {}^{1,3}Q_e. \qquad (10a)$$

When a CTC of the type $^1(S.A)_0$ participates in the electron transfer, photoprocesses (X), analogous to (IX), proceed in accordance with Scheme (II) (with replacement of D by S and of S by A). The free energy of electron phototransfer is (Fig.1b)

$$\Delta G_{23}(X) = e\{E'_{1/2}(^1D_0/D^{+\cdot}) - E'_{1/2}[(SA^{-\cdot})/^{1,3}(S^{+\cdot}A^{-\cdot})_1]\}, \qquad (16)$$

where

$$E'_{1/2}[(SA^{-\cdot})/^{1,3}(S^{+\cdot}A^{-\cdot})_1] = eE'_{1/2}[(SA^{-\cdot})/^1(SA)_0] + {}^{1,3}E_{00};$$
$$eE'_{1/2}[(SA^{-\cdot})/^1S.A_0)] = eE'_{1/2}(A^{-\cdot}/^1A_0) - X;$$
$$^{1,3}E_{00} = e[E'_{1/2}(^1S_0/S^{+\cdot}) - E'_{1/2}(A^{-\cdot}/^1A_0)] + \Delta G^P_{CTC} + X + {}^{1,3}Q_e.$$

After substitutions, Eqn.(16) becomes

$$\Delta G_{23}(X) = e[E_{1/2}(^1D_0/D^{+\cdot}) - E_{1/2}(^1S_0/S^{+\cdot})] - \Delta G^P_{CTC} - {}^{1,3}Q_e.$$

We shall now proceed to the consideration of reactions (III) to (V) of the photoexcited sensitiser. The electron phototransfer reactions involving a sensitiser which does not form complexes with D or A components in the ground state are considered below. Spectral sensitisation is in this case caused by the formation of the collision complex between the photoexcited sensitiser and the D and A components of the system. It is shown below that the direction of the charge transfer process (the type of primary reaction) is determined by the relative positions of the levels of the photoexcited sensitiser and the equilibrium redox potential of the components of the EDA system.

We shall now examine the primary oxidation of the donor and the reduction of the excited sensitiser [reactions (III) to (V)]:

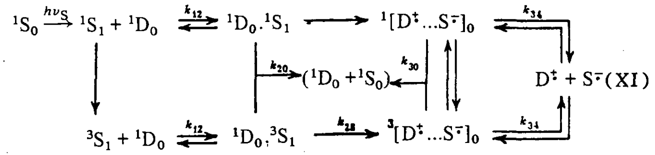


Fig.2*a* shows that reaction (XI) in stage 23 is determined by the shift of the reduction potential of the sensitiser in the excited state in the positive direction up to the value (in the polymer composition)

$$eE'_{1/2}(S^{-\cdot}/^{1,3}S_1) = eE_{1/2}(S^{-\cdot}/^1S_0) - \Delta G^-_p + {}^{1,3}E_{00}\ (\text{or } {}^{1,3}E). \qquad (17)$$

The potential defined by Eqn.(17) corresponds to equilibrium if the electron transfer reaction takes place after the transitions of $^{1,3}S_1$ to the lowest excited singlet or triplet level ($^{1,3}E_{00}$).

The free energy of electron transfer (stage 23) in reaction (XI) is

$$\Delta G_{23}(XI) = e[E_{1/2}(^1D_0/D^{+\cdot}) - E_{1/2}(S^{-\cdot}/^1S_0)] + 2\Delta G^+_p - \frac{e^2}{R\kappa} - {}^{1,3}E_{00}, \qquad (18)$$

where R is the distance between $D^{+\cdot}$ and $S^{-\cdot}$ in the geminal pair. It has been suggested that, in contrast to the excited CTC, for example $^{1,3}(D^{+\cdot}S^{-\cdot})_1$, polarising the medium as a single dipole [see Eqn.(12)], the geminal pair $^{1,3}[D^{+\cdot}...S^{-\cdot}]_0$ corresponds to the Coulombic attraction ($e^2/R\kappa$) of the radical-ions having their own solvation shells.

The free energy of the secondary reaction

$$S^{-\cdot} + {}^1A_0 \rightleftarrows {}^1S_0 + A^{-\cdot} \qquad (XII)$$

is defined as the difference between the following equilibrium redox potentials:

$$\Delta G_{sec}(XII) = e[E_{1/2}(S^{-\cdot}/^1S_0) - E_{1/2}(A^{-\cdot}/^1A_0)]. \qquad (19)$$

In the primary reduction of the acceptor as a result of the oxidation of the photoexcited sensitiser [reaction (IV)], processes (XIII) and (XIV) (Fig.2*b*), analogous to processes (XI and (XIX) (with the replacement of D by S and of S by A), take place.

The free energy of electron transfer via reaction (XIII) is (Fig. 2*b*)

$$\Delta G_{23}(\mathrm{XIII}) = e[E_{1/2}(^1\mathrm{S}_0/\mathrm{S}^{\cdot+}) - E_{1/2}(\mathrm{A}^{\cdot-}/^1\mathrm{A}_0)] + 2\Delta G_\mathrm{p}^{\pm} - \frac{e^2}{R\kappa} - {}^{1,3}E_{00}, \quad (20)$$

while that of electron transfer via reaction (XIV) is given by

$$\Delta G_\mathrm{sec}(\mathrm{XIV}) = e[E_{1/2}(^1\mathrm{D}_0/\mathrm{D}^{\cdot+}) - E_{1/2}(^1\mathrm{S}_0/\mathrm{S}^{+})]. \quad (21)$$

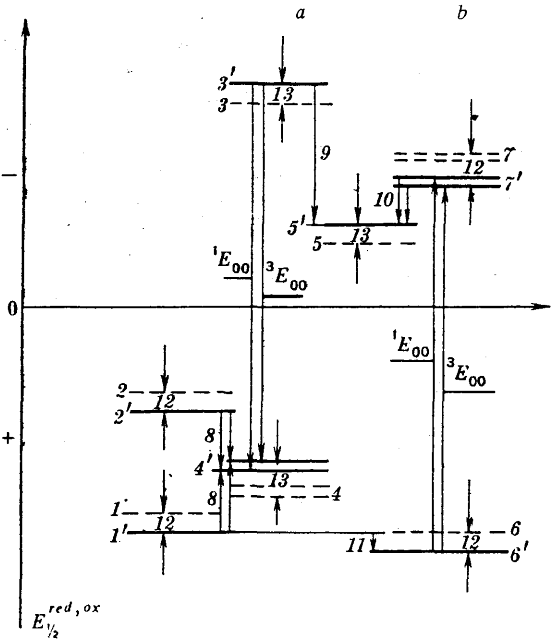


Figure 2. Schematic illustration of the relative positions of the oxidation-reduction potentials in the primary donor oxidation (*a*) and acceptor reduction (*b*) reactions; D and D′ = donors of different nature: *1*) and *1′*) $E_{1/2}(^1\mathrm{D}_0/\mathrm{D}^{\cdot+})$, $E'_{1/2}(^1\mathrm{D}_0/\mathrm{D}^{\cdot+})$; *2*) and *2′*) $E_{1/2}(^1\mathrm{D})'_0/(\mathrm{D}')^{\cdot+}$, $E'_{1/2}[^1(\mathrm{D}')_0/(\mathrm{D}')^{\cdot+}]$; *3*) and *3′*) $E_{1/2}(\mathrm{S}^{\cdot-}/^1\mathrm{S}_0)$, $E'_{1/2}(\mathrm{S}^{\cdot-}/^1\mathrm{S}_0)$; *4*) and *4′*) $E_{1/2}(\mathrm{S}^{\cdot-}/^{1,3}\mathrm{S}_1)$, $E'_{1/2}(\mathrm{S}^{\cdot-}/^{1,3}\mathrm{S}_1)$; *5*) and *5′*) $E_{1/2}(\mathrm{A}^{\cdot-}/^1\mathrm{A}_0)$, $E'_{1/2}(\mathrm{A}^{\cdot-}/^1\mathrm{A}_0)$; *6*) and *6′*) $E_{1/2}(^1\mathrm{S}_0/\mathrm{S}^{\cdot+})$, $E'_{1/2}(^1\mathrm{S}_0/\mathrm{S}^{\cdot+})$; *7*) and *7′*) $E_{1/2}(^{1,3}\mathrm{S}_1/\mathrm{S}^{\cdot+})$, $E'_{1/2}(^{1,3}\mathrm{S}_1/\mathrm{S}^{\cdot+})$; *8*) ΔG_{23} (XI); *9*) ΔG_sec (XII); *10*) ΔG_{23} (XIII); *11*) ΔG_sec (XIV); *12*) ΔG_p^{+}; *13*) ΔG_p^{-}.

The dominant direction of the primary reaction is determined by the difference between free energies $\Delta G_{23}(\mathrm{XI})$ to $\Delta G_{23}(\mathrm{XIII})$ and the ratio of the equilibrium concentrations is given by the expression

$$\frac{^{1,3}[\mathrm{D}^{\cdot+}\mathrm{S}^{\cdot-}]_1}{^{1,3}[\mathrm{S}^{\cdot+}\mathrm{A}^{\cdot-}]_1} = \exp\left[\frac{\Delta G_{23}(\mathrm{XI}) - \Delta G_{23}(\mathrm{XIII})}{kT}\right]$$

The collision of $^{1,3}\mathrm{S}_1$ (energy $^{1,3}E_{00}$) with the complex $^1(\mathrm{D.A})_0$ entails two possible reaction pathways (*a* or *b*):

$$\begin{tikzcd}
{^{1,3}\mathrm{S}_1 + {}^1(\mathrm{D.A})_0} \arrow[r] & {^{1,3}\mathrm{S}_1.{}^1(\mathrm{D.A})_0} \arrow[r, "d"] \arrow[d, "b"] & {^{1,3}[\mathrm{D}^{\cdot+}\mathrm{A}\ldots\mathrm{S}^{\cdot-}]_0,} \arrow[d] & {\mathrm{D}^{\cdot+} + \mathrm{A}^{\cdot-};} \\
 & {^{1,3}[\mathrm{S}^{\cdot+}\ldots\mathrm{DA}^{\cdot-}]_0} \arrow[r] & {^{1,3}[\mathrm{D}^{\cdot+}\ldots\mathrm{A}^{\cdot-}]_0} \arrow[r] \arrow[ur] \arrow[dr] & {\mathrm{D}_1^{+} + \mathrm{A}_1^{-},} \\
 & & & {^1(\mathrm{D.A})_0,}
\end{tikzcd}$$

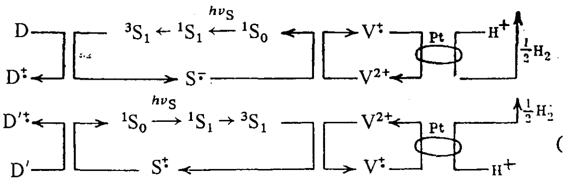
for which

$$\Delta G(a) = e[E_{1/2}(^1\mathrm{D}_0/\mathrm{D}^{\cdot+}) - E_{1/2}(\mathrm{S}^{\cdot-}/^1\mathrm{S}_0)] + 2\Delta G_\mathrm{p}^{\pm} + X + {}^{1,3}E_{00},$$
$$\Delta G(b) = e[E_{1/2}(^1\mathrm{S}_0/\mathrm{S}^{\cdot+}) - E_{1/2}(\mathrm{A}^{\cdot-}/^1\mathrm{A}_0)] + 2\Delta G_\mathrm{p}^{\pm} + X - {}^{1,3}E_{00}.$$

The dominant pathway is determined by the difference $\Delta G(a) - \Delta G(b)$:

$$\frac{^{1,3}[\mathrm{D}^{\cdot+}\mathrm{A}\ldots\mathrm{S}^{\cdot-}]_0}{^{1,3}[\mathrm{S}^{\cdot+}\ldots\mathrm{DA}^{\cdot-}]_0} = \exp\,[\Delta G(a) - \Delta G(b)]/kT.$$

Liquid-phase systems incorporating donors of different nature (D and D′), sensitisers comprising low-molecular-weight and high-molecular-weight derivatives $\mathrm{Ru(bipy)}_3^{2+}$, xanthene dyes, and porphyrins, and acceptors comprising the viologens (V^{2+}) in the presence of dispersed platinum have been investigated in detail[8-11,71,91-96] in connection with the development of converters of solar radiation into the chemical energy of the evolution of molecular hydrogen. The set of reactions can be represented by two schemes:



(XV)

(XVI)

In reactions (XV) and (XVI) the free energy of formation of H_2 is

$$\Delta G(\mathrm{H}_2) = e[E_{1/2}(\mathrm{V}^{\cdot+}/\mathrm{V}^{2+}) - E_{1/2}(0.5\mathrm{H}_2/\mathrm{H}^+)]$$

where $E_{1/2}(0.5\mathrm{H}_2/\mathrm{H}^+) = -0.059\mathrm{pH}$ V (n.h.e.) is the equilibrium potential of the reduction of H^+ to $0.5\mathrm{H}_2$ in the reaction $0.5\mathrm{H}_2 \rightleftharpoons \mathrm{H}^+ + e$ on the platinum surface.

A high quantum yield of H_2 [$\phi(0.5\mathrm{H}_2) = 0.25$] has been attained in a composition where S was a complex system comprising a mixture of three xanthene dyes with different regions of optical absorption which transmit the absorbed solar energy to the "aerial"— anthracene-9-carboxylic acid. The "aerial" in the excited triplet state participates in electron transfer from the donor [ethylenediaminetetraacetic acid (EDTA)] to the acceptor—methylviologen.[96]

Fig. 2 shows that the position of the ground energy level of the sensitiser, for example, the ruthenium complex $\mathrm{Ru(bipy)}_3^{2+}$, is characterised by two redox potentials:[71]

$$eE_{1/2}\{\mathrm{Ru(bipy)}_3^{1+}/^3[\mathrm{Ru(bipy)}_3^{2+}]_1\} =$$
$$= eE_{1/2}\{\mathrm{Ru(bipy)}_3^{1+}/^1[\mathrm{Ru(bipy)}_3^{2+}]_0\} + {}^3E_{00} = 0.84 \text{ eV} \quad (22)$$
$$({}^3E_{00} = 2.1 \text{ eV})$$
$$eE_{1/2}\{^1[\mathrm{Ru(bipy)}_3^{2+}]_0/\mathrm{Ru(bipy)}_3^{3+}\} = 1.27 \text{ eV (n.h.e.)}.$$

which determine the free energies of electron transfer in the interaction with the donor. The first value characterises the free energy, defined by Eqn. (18), of electron transfer from D to the lowest level of the triplet-excited sensitiser [reaction (XV)] and the second corresponds to the free energy, defined by Eqn. (21), of the secondary reaction (XVI) involving electron transfer from D′ to the oxidised sensitiser.

The position of the excited energy level of the sensitiser is characterised analogously by the redox potentials[71]

$$eE_{1/2}\{^3[\mathrm{Ru(bipy)}_3^{2+}]_1/\mathrm{Ru(bipy)}_3^{3+}\} =$$
$$= eE_{1/2}\{^1[\mathrm{Ru(bipy)}_3^{2+}]_0/\mathrm{Ru(bipy)}_3^{3+}\} - {}^3E_{00} = -0.83 \text{ eV};$$
$$eE_{1/2}\{\mathrm{Ru(bipy)}_3^{1+}/^1[\mathrm{Ru(bipy)}_3^{2+}]_0\} = -1.26 \text{ eV (n.h.e.)}.$$

which determines the free energies, defined by Eqns. (20) and (19), of electron transfer to the acceptor respectively from the excited ruthenium complex in the primary reaction (XVI) and from the reduced sensitiser in the secondary reaction tion (XV). Reaction (XV) predominates when donors with a low value of $E_{1/2}({}^1D_0/D^{\dot{+}})$ [0.16–0.64 V (n.h.e.)] are used, such as tetramethyl-p-phenylenediamine, diphenyl-p-phenylenediamine, tetramethylbenzidine, and tetrapyrenediamine, in combination with $Ru(bipy)_3^{2+}$ and methylviologen (MV^{2+}) as the acceptor: $E_{1/2}(MV^{\dot{+}}/MV^{2+}) = -0.44$ V (n.h.e). Reaction (XVI) proceeds in the presence of donors such as triethanolamine (TEOA) and EDTA, whose equilibrium oxidation potentials are $E_{1/2}[({}^1D')_0/(D')^{\dot{+}}] = 0.82$ and 0.9 V (n.h.e.) respectively and are almost identical with or more positive than the potential defined by Eqn.(22).

The positions of the energy levels of the sensitised dyes (azine, thiazine, and xanthene dyes) and donors (EDTA and TEOA) depend on the acid–base properties of the medium.[76, 97–100] For example, the thiazine dyes (Dy^+), thionine (TH^+) and Mb^+, widely used in non-silver information recording processes, have an equilibrium reduction potential in their protonated form which is more positive than in the non-protonated form by the amount

$$E_{1/2}(DyH^{\dot{+}}/{}^1(DyH^{2+})_0 - E_{1/2}(Dy^{\cdot}/{}^1(Dy^+)_0 =$$
$$2.303\,\frac{kT}{e}\,(pK_s - pK_a),\ (2.303\,\frac{kT}{e} = 0.059,\ V,\ at\ 293\ K),$$

where K_s and K_a are the equilibrium constants of the reactions

$$DyH^+ \overset{K_s}{\rightleftarrows} Dy + H^+ \text{ and } DyH^{2+} \overset{K_a}{\rightleftarrows} Dy^+ + H^+.$$

The quantities pK_s and pK_a are 10.4 and −0.4 for thionine and 9 and 0 respectively for Methylene Blue. The equilibrium potentials of the reduction of the triplet-excited dyes are more positive in the protonated form than in the non-protonated form by the amount

$$E_{1/2}(DyH^{\dot{+}}/{}^3(DyH^{2+})_1] - E_{1/2}[Dy^{\cdot}/{}^3(Dy^+)_1] = 0.059\,(pK_s - pK_t),$$

where K_t is the equilibrium constant of the reaction

$${}^3(DyH^{2+})_1 \overset{K_t}{\rightleftarrows} {}^3(Dy^+)_1 + H^+,$$

amounting to 7.0 and 7.2 respectively for TH^+ and Mb^+.

The decrease (shift in the positive direction) of the energy levels of the triplet-excited dyes on protonation increases the free energy (rate constant) for electron transfer from the donor to the photoexcited dye.

3. Methods of Limiting the Reverse Reactions

The suppression of the reverse reactions is one of the central problems for the practical realisation of electron transfer processes in systems incorporating CTC. In photoconducting systems, the suppression of the reverse reactions (recombination in geminal pairs) increases the quantum efficiency of the generation of free charge carriers. This can be achieved by applying strong electric fields or, for example, in the case of PVCA, by increasing the initial distance separating the charges in the geminal pair by increasing the energy of the excited quanta.[1,3]

In non-silver light-sensitive systems based on CTC, halogen-containing compounds (CBr_4, $CBr_3SO_2CBr_3$) are used as acceptors. The reverse reaction is quenched as a result of the dissociation of the acceptor on electron capture ($CBr_4 + e \rightarrow Br^- \ldots \dot{C}Br_3$; $CBr_3SO_2CBr_3 + e \rightarrow Br^- \ldots \dot{C}Br_2SO_2.CBr_3$, etc.). In sensitised systems based on viologens as acceptors one uses donors and conditions where the radical-cationic forms, formed as a result of the electron transfer reactions, are deprotonated [$DH^+ \rightarrow D^{\bullet} + H^+$ ($PVA^{\dot{+}}$,[3,101] $TEOA^{\dot{+}}$,[102,103] $EDTA^{\dot{+}}$ [104,105])]. In contrast to DH^+, the radicals $D^{\bullet}$ [$-CH-\dot{C}OH-$($PVA^{\bullet}$), $(CH_2OHCH_2)_2NCH_2\dot{C}HOH$ or $(CH_2.OHCH_2)_2N\dot{C}HCH_2OH$ ($TEOA^{\bullet}$), $R_2N-(CH_2)_2-(R)N-\dot{C}HCOO^-H^+$ with $R \equiv CH_2COO^-H^+$ ($EDTA^{\bullet}$)] are strong donors and effect additional electron transfer to the acceptor under dark conditions, accompanied by the irreversible formation of the carbonyl groups $-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-$ in PVA [3,101] and also of unstable imino-forms $\gt\overset{+}{N}=CH-CH_2OH$ or $-\underset{\underset{\displaystyle R}{|}}{\overset{+}{N}}=CHCOO^-H^+$ in TEOA [102] or EDTA,[105] which undergo subsequent irreversible decomposition. Thus in systems of this kind not only are the reverse reactions suppressed but the quantum yield of the reduced viologen is also doubled. In polymer systems the doubling of $\phi(V^{\dot{+}})$ is attained by the conversion of low-molecular-weight acceptors into polymeric forms with a high local concentration of viologen units, such as polypentamethyleneviologen, polydecamethyleneviologen, or poly-p-xylyleneviologen.[3,101,106]

According to Ohsako et al.[107], the polymer based on polystyrene with viologen substituents in the phenyl group [PV^{2+}: $E_{1/2}(PV^{\dot{+}}/PV^{2+}) = -0.135$ V (n.h.e.)] does not enter into a redox interaction either with the excited or the oxidised complex $Ru(bipy)_3^{2+}$ apparently due to steric hindrance. Electron phototransfer takes place after the additional introduction into the system of electron transferring agents (ET), for example, dipropyl-4,4'–dipyridylsulphonate [$E_{1/2}(ET^{\dot{-}}/ET) = -0.68$ V (n.h.e.)]. The charge transfer

$${}^3[Ru(bipy)_3^{2+}]_1 + ET \rightarrow Ru(bipy)_3^{3+} + ET^{\dot{-}},$$

which takes place after electron phototransfer via the reaction

$$ET^{\dot{-}} + PV^{2+} \rightarrow ET + PV^{\dot{+}},$$

effectively competes with the reverse reaction

$$ET^{\dot{-}} + Ru(bipy)_3^{3+} \rightarrow ET + Ru(bipy)_3^{2+},$$

ensuring a PV^+ lifetime of ~1.2 s and a ~50-fold increase of $\phi(PV^{\dot{+}})$ compared with $\phi(ET^{\dot{-}}) = 0.12 \times 10^{-2}$ in the absence of PV^{2+}.

In order to separate the reaction products in liquid media, use is made of micellar solutions, two-layer membranes,[9,10] and the components at the interface in the field of a negatively charged dispersed SiO_2.[108,109]

4. Oxidation-Reduction Potentials and Optical Transition Energies

The relation between the redox potentials, the electronic transition energies, and the positions of the highest occupied (ε_1) and lowest unoccupied (ε_2) orbitals, calculated by quantum-chemical methods (mainly the Hückel molecular orbital method: HMO) has been discussed in monographs[6,110,111] and in a large number of original and new communications in relation to polyenes and aromatic hydrocarbons,[110–113] heterocyclic compounds,[68,112,114] and dyes of different classes (palmitic, thiazine, oxazine, acridine, and xanthene dyes, aza-pigments, etc).[6,7,69,72,73,112,115,116] It has been demonstrated in monographs[110,111] in relation to a large number of polyenes and aromatic hydrocarbons that, for compounds of the same class, there is a linear relation between the experimental $E_{1/2}^{ox}$ (or I_M), $E_{1/2}^{red}$ (or E_M), and the values of m_1 and m_2, characterising the coefficients of the orbitals and calculated by the HMO method:

$$\varepsilon_1 = \alpha + \beta_0 m_1, \quad \varepsilon_2 = \alpha - \beta_0 m_2$$

where α and β_0 are the Coulombic and resonance integrals.

The following linear relations have been established:

$$E_{1/2}(\mathrm{M/M^{\ddagger}}) = \beta_1 m_1 + c$$

or [see Eqn.(4b)]

$$I_M = \beta_1 m_1 + c_1,$$

and also

$$E_{1/2}(\mathrm{M^{\mp}/M}) = -\beta_2 m_2 + c_2$$

or [see Eqn.(5b)]

$$E_M = -\beta_2 m_2 + c_3,$$

where $c - c_3$ are constants.

The following correlation has been derived:[6,7,72,73,115,116]

$$h\nu_{\max,\exp} = \beta_3(m_1 - m_2).$$

A linear relation has been proposed for aromatic hydrocarbons:[112]

$${}^3E_{00} = \beta_4(m_1 - m_2)$$

where $\beta_1 - \beta_4$ are correlation parameters relating the experimental and calculated quantities.

The relations between the positions of the energy levels and the calculated values for dyes have been subjected to a detailed analysis[68,69] on the basis of correlations:[114]

$${}^1E_{00} = \beta_5(m_1 - m_2) - J_{12} + 2K_{12} \tag{23}$$

$${}^3E_{00} = \beta_5(m_1 - m_2) - J_{12} \tag{24}$$

$$e[E_{1/2}({}^1\mathrm{M_0/M^{\ddagger}}) - E_{1/2}(\mathrm{M^{\mp}}/{}^1\mathrm{M_0})] = \beta_5(m_1 - m_2). \tag{25}$$

According to Eqns.(23)—(25), the difference between the redox potentials defined by Eqn. (25) can be regarded as the experimental distance between the half-filled orbitals ε_1 and ε_2 in the absence of electron-electron interaction. The occurrence of electronic interaction under the conditions of the photoexcitation of the molecule ($-J_{12} + 2K_{12}$ for the excited singlet state and $-J_{12}$ for the excited triplet state) should entail the appearance of the following relations:

$${}^1E_{00} = e[E_{1/2}({}^1\mathrm{M_0/M^{\ddagger}}) - E_{1/2}(\mathrm{M^{\mp}}/{}^1\mathrm{M_0})] - J_{12} + 2K_{12}, \tag{26}$$

$${}^3E_{00} = e[E_{1/2}({}^1\mathrm{M_0/M^{\ddagger}}) - E_{1/2}(\mathrm{M^{\mp}}/{}^1\mathrm{M_0})] - J_{12}. \tag{27}$$

In related series, such as those of aromatic compounds, mono-aza-compounds, and poly-*N*-heterocyclic compounds, an increase in molecular size leads simultaneously to a decrease of both J_{12} and of the polarisation energy $P^{\pm}$.[110] The experimental relations[68,112]

$$J_{12} = a + be[E_{1/2}(\mathrm{M/M^{\ddagger}}) - E_{1/2}(\mathrm{M^{\mp}/M})], \tag{28}$$

$${}^3E_{00} = (1 - b)e[E_{1/2}(\mathrm{M/M^{\ddagger}}) - E_{1/2}(\mathrm{M^{\mp}/M})] - a. \tag{29}$$

are linked to these changes. Table 1 presents the experimental constants $-J_{12} + 2K_{12}$, $1 - b$, and a in Eqns.(26) and (29) for a series of related compounds. Deviations from the common relations (26) and (29) are characteristic of molecules with either complex substituting groups or with variable conformations, which requires allowance for additional intramolecular interactions between non-neighbouring atoms.[110,111] It has been suggested[117] that the optical absorption energy of cyanine dyes be related to the redox-potentials by means of the formula [1 : 1 (vol.%) water—methanol mixture]:

$$h\nu_{\max} = 0.87e[E_{1/2}(\mathrm{S/S^{\ddagger}}) - E_{1/2}(\mathrm{S^{\mp}/S})],\ \mathrm{eV}.$$

The relation (in aqueous methanolic solutions)

$${}^1E_{00} = e[E_{1/2}({}^1\mathrm{S_0/S^{\ddagger}}) - E_{1/2}(\mathrm{S^{\mp}}/{}^1\mathrm{S_0})] + 0.37,\ \mathrm{eV}, \tag{30}$$

or

$${}^1E_{00} = I_S^{\mathrm{gas}} - E_S^{\mathrm{gas}} - 3.28,\ \mathrm{eV}, \tag{31}$$

has been obtained[69] for 100 sensitising dyes (mainly cyanine dyes—90 compounds, and also xanthene and thiazine dyes, and individual representatives of the groups of acridine, oxazine, and alloxazine dyes), which have been investigated in detail in connection with their use in the silver halide and non-silver photographic processes and in the development of photovoltaic cells. According to literature data, the splitting $S_1 - T_1$ is $2K_{12} \doteq 0.27$ eV for cyanine dyes,[90] ~0.32 eV, for acryidine dyes,[118] and ~0.31 eV for xanthene dyes.[118] We find from Eqns.(26) and (30) that the interelectron repulsion energy is small: $-J_{12} = +0.37 - 2K_{12} = 0.37 - (0.27\text{–}0.32) = +0.1\text{–}0.05$ eV. Thus, for sensitising dyes, we have

$${}^3E_{00} = e[E_{1/2}({}^1\mathrm{S_0/S^{\ddagger}}) - E_{1/2}(\mathrm{S^{\mp}}/{}^1\mathrm{S_0})] + (\leqslant 0.1),\ \mathrm{eV}; \tag{32}$$

for this series of compounds, we have the coefficients $b \cong 0$ and $a \cong -0.1$ eV in Eqn.(29) (Table 1).

Table 1. The coefficients $-J_{12} + 2K_{12}$, $1 - b$, and a in Eqns.(26) and (29) for a series of related compounds (aqueous and methanol solutions).[112]

Coefficient	Aromatic hydrocarbons	Mono-*N*-heterocyclic compounds ($n \rightarrow \pi^*$ transition)	Poly-*N*-heterocyclic compounds ($\pi \rightarrow \pi^*$ transition)	Dyes*
$-J_{12}+2K_{12}$	—	—	0.3	0.37**
$(1-b)$	0.82	0.88	0.9	1.0**
a	0.52	0.54	0.687	—0.1***

*Cyanine, acridine, thiazine, oxazine, xanthene, etc. dyes (100 compounds in all).[69]

**Data of Loutfy and Sharp.[69]

***Calculated by the authors of the review.

Table 2. Electrochemical and spectral characteristics of the additives and the energy characteristics of the photovoltaic cells based on Phtc.[34]

Additive	$E_{1/2}^{red}$	$E_{1/2}^{ox}$	Absorption		φ	η' %
	volts (sat.c.e.)		$\lambda_{\max}$, nm	$\epsilon_{\max}$, dm^3 mol^{-1}cm^{-1}		
TMF*	—0.42	1.5	370	$1\cdot10^4$	0.93	1.58
Coumarin 6	—1.50	1.16	480	$1\cdot10^5$	0.84	1.54
Rubrene	—1,55	0.86	525	$1{,}2\cdot10^5$	0.76	1.44
Rhodamine 6G	—0.84	1.30	545	$1.2\cdot10^5$	0.40	1.00
Perylene	—1.72	1.06	440	$3.4\cdot10^4$	0.33	0.48
Phtc without additives	—1.24	0.90	—	—	0.27	0.50
DPBF**	—1.98	0.73	420	$1\cdot10^4$	0.14	0.27
BPEA***	—1.40	1.22	470	$3.4\cdot10^4$	0.04	0.06
Safranine	—	0.5	—	—	0.02	0.02

*Trinitrofluorenone. **1,4-Diphenyl-2,3-benzofuran. ***9,10-Bi(phenylethynyl)anthracene.

5. The Mechanisms of the Spectral Sensitisation of the Photoelectric Sensitivity in Photovoltaic Cells

In the study of the processes in photovoltaic cells based on Phtc dispersed in a polymer matrix,[34,46-48] the positions of the levels of the additives adsorbed on the surfaces of the Phtc particles were estimated from electrochemical data, which, together with spectral and energy characteristics, are listed in Table 2. Polycarbonate was used as the polymer matrix in the photovoltaic cell. The quantity ϕ was determined from Eqn.(3) for $\lambda = 620$ nm and $L_T = 0.1$ mW cm^{-2}. The efficiency η' [see Eqn.(2)] was measured with exposure to sunlight; $L_T = 1$ mW cm^{-2}.

In a layer without additives, the charge carriers are generated at the Schottky barrier in accordance with the scheme in Fig.3*a*. The electron-hole pair formed in the region of the Schottky barrier dissociates in the barrier electric field, the electron passing to the metal and the hole drifting into the bulk of the Phtc. If the added substance S has an oxidation potential satisfying the condition $E_{1/2}\cdot$ $\cdot({}^1S_0/S^{\dot{+}}) < E_{1/2}({}^1Phtc_0/Phtc^{\dot{+}})$, then it captures a hole and functions as a densensitiser (Fig.3*b*):

$$S + Phtc^{\dot{+}}(hole) \rightarrow S^{\dot{+}} + Phtc.$$

The hole does not then escape into the bulk phase but is trapped by the additive molecule, which sharply increases the probability of its recombination with an electron and leads to a decrease of the photocurrent compared with the initial layer. Among the additives listed in Table 2, safranine and DPBF satisfy this condition. The densensitising effect of BPEA may be determined by the tendency of this substance to aggregate with formation of insulating layers on the Phtc grains, which diminish I_{SC}.

In a solid, the absorption of light by Phtc particles leads to the formation of the exciton state ${}^1Phtc_1$, which diffuses to the Phtc/S interface and forms an exciplex with a molecule of the additive, which can decompose into charged species, the process intensifying in an electric field (E_d):

$${}^1Phtc_1 + {}^1S_0 \rightarrow {}^1(Phtc.S)_1 \rightarrow {}^1(Phtc^{\dot{+}}S^{\dot{-}})_1 \xrightarrow{E_d} Phtc^{\dot{+}} + S^{\dot{-}}.$$

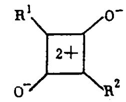
The free holes Phtc$^+$ escape into the bulk of the phthalocyanine particle and the reduced molecule of the additive gives up an electron to the metal (Fig.3*c*). This chemical sensitisation process constitutes an additional channel to the formation of free separated charge carriers and to the increase of J_{SC}.

In spectral sensitisation (Fig.3*d*), the additive molecule absorbs light. For effective spectral sensitisation, it is essential that the excited additive molecule should accept an electron from Phtc. The relation between the electrochemical and spectral parameters of the additive is given[34] by Eqn.(26) on the assumption that $-J_{12} + 2K_{12} \cong 0$, i.e. that the reduction potential of the excited additive molecule is equal to the oxidation potential of the molecule in the ground state. According to Table 2, almost all additives in their excited states, with the exception of DPBF and safranine, are capable of injecting holes into (of capturing electrons in) the bulk of the semiconductor Phtc and thus of effecting spectral sensitisation. In reality, spectral sensitisation was a maximum for coumarin 6 or rhodamine 6G and was weaker for rubrene and perylene, while DPBF, BPEA, and safranine did not influence the photosensitivity of Phtc. The agreement between experiment and the mechanism considered, involving charge transfer, does not rule out the contribution to the spectral sensitisation by processes involving the transfer of excitation energy from the additive to Phtc.

The study[119] of the photovoltaic effect in the cells

Al/the dye I dispersed in the polymer/SnO_2 – Sb

showed that I_{SC} is smaller by four orders of magnitude than in the cells based on sensitised Phtc. Here the dye I has the structure



R^1 and R^2 are radicals derived from anilines, indoles, azulenes, indolizines, and methines.

6. Spectral Sensitisation of Non-silver CTC-based Photographic Systems by Cyanine Dyes

Cyanine dyes, which have a large extinction coefficient, a small $S_1 - T_1$ splitting, and hence a short lifetime in the excited singlet state, enter into photochemical reactions in the excited triplet state.[85,87,90]

Table 3 presents the characteristics of cyanine dyes, which, as mentioned above (Section II), have been investigated as sensitisers of non-silver photographic polymeric layers based on the CTC of benzyldiphenylamine (Am) as the donor and acceptors (A = CBr_4 or $CBr_3SO_2CBr_3$). These polymeric layers are sensitive to light at wavelengths $\lambda \leq 500$ nm as a consequence of the optical absorption of A and Am in the region up to ~320 nm and of the CTC in the range 320–500 nm. The coloured product ($Am_1^{\dot{+}}$), which is assumed to have the structure

$$(C_6H_5)_2\overset{+}{N}{=}CH{-}C_6H_5 \qquad \text{(XVII)}$$

is formed under the influence of light.

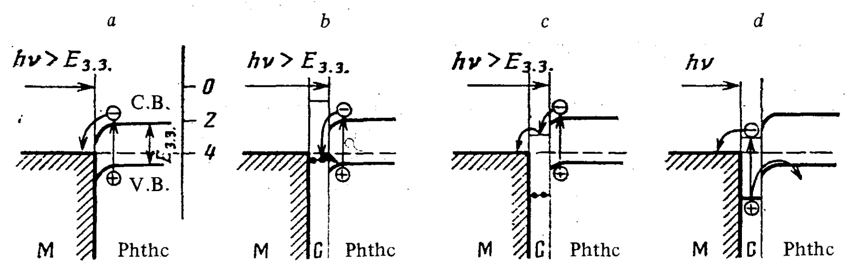


Figure 3. Schematic illustration of the generation of charge carriers (holes) at the Schottky barrier in the M/Phtc (dispersed in polycarbonate) photovoltaic cell; *a*) no additives; *b*) desensitisation by added safranine and DPBF; *c*) chemical sensitisation by added TNF and coumarin 6; *d*) spectral sensitisation by added rhodamine 6G, coumarin 6, etc.; M = metallic semitransparent layer; C.B. = conductivity band; V.B. = valence band; $E_{f.g.}$ = width of the forbidden gap of Phtc.[34]

When cyanine dyes are introduced, processes of three types take place:

(1) Dyes with $E_{1/2}(^1S_0/S^{+\cdot}) < 0.5$ V (sat.c.e.) are decolorised in the dark on contact with acceptors.

(2) Dyes having $E^{ox}_{1/2}$ in the range $0.5 < E^{ox}_{1/2} < 0.9$ V (sat.c.e) are decolorised as a result of photoexcitation on contact with A (Fig.4*a*), the efficiency of the process increasing with decrease of $E_{1/2}(^1S_0/S^{+\cdot})$. Such dyes are weak spectral sensitisers of compositions incorporating the complexes Am.A. It has been established[3, Ch.5; 49,50] that the quantum yield of the decolorisation of dyes increases linearly with acceptor concentration: $\phi_{dec} = a[A]$, where $A = CBr_4$ or $CBr_3SO_2CBr_3$.

Table 3. The structural formulae of the dyes, the potentials $E^{ox}_{1/2}$ and $E^{red}_{1/2}$ (sat.c.e.) measured in acetonitrile[49] and in the 1 : 1 (vol.%) $C_2H_5OH-H_2O$ mixture at pH 10–12,[72,73] and the values of λ_{max} in a CPVC film.[49]

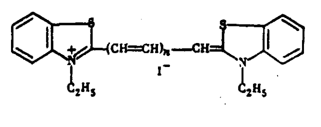
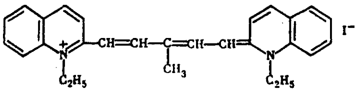
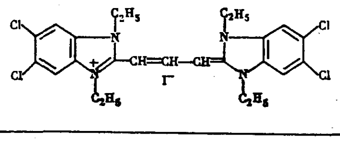
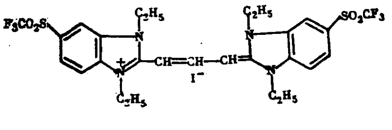
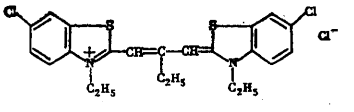
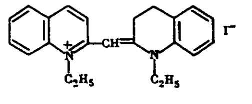
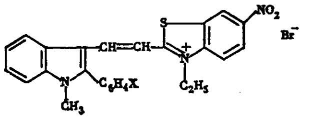
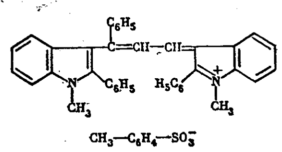
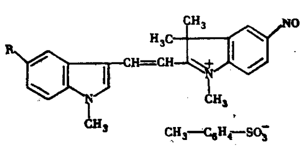
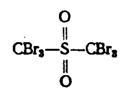
No.	Dye (S)	$E_{1/2}(S/S^{+\cdot})$, V	$E_{1/2}(S^{-\cdot}/S)$, V	λ_{max}, nm	Refs.
1	 $n = 5$	0.03	−0.6	1020	[49]
		—	−0.7	—	[72]
2	$n = 4$	0.12	−0.68	874	[49]
			−0.8		[72, 73]
3	$n = 3$	0.26	−0.8	762	[49, 72, 73]
4	$n = 2$	0.48	−0.93	656	[49, 72]
5	$n = 1$	0.71	−1.1	560	[6, 72]
6		—	—	740	[49]
7		0.55	−1.62	522	[49]
8		0.73	−1.42	531	[49]
9		0.90	−0.94	571	[49]
10		0.99	−1.03	—	[6]
		0.9	−1.15	531	[49]
11	 X=H	0.90	−0.65	535	[49]
12	X=CH_3	0.93	−0.58	535	[49]
13	X=Br	1.18	−0.42	538	[49]

Table 3 (contd.).

No.	Dye (S)	$E_{1/2}(S/S^{+\cdot})$, V	$E_{1/2}(S^{-\cdot}/S)$, V	λ_{max}, nm	Refs.
14		1.0	−0.5	630	[120]
15	 R=H	1.1	−0.55	530	[120]
16	R=NO_2	1.35	−0.65	540	[49]
17	$(C_6H_5)_2N-CH_2-C_6H_5$	0.98	—	296**	[49]
18	CBr_4	—	−0.7*	240**	[49]
19	 $CBr_3-\overset{\overset{\displaystyle O}{\Vert}}{\underset{\underset{\displaystyle O}{\Vert}}{S}}-CBr_3$	—	−0.6*	238** (shoulder at 265)	[50]

Remarks. *Calculated by Eqn.(5b) from $E_A(CBr_4) = 2.0$ eV and $E_A(CBr_3SO_2CBr_3) = 2.1$ eV.[50] **Measured in ethanol.

The type of decolorisation of group 1 and 2 dyes described justifies the conclusion[3, Ch.5; 49,50] that the decolorisation is determined by electron-donating properties.

(3) Dyes with $E_{1/2}(^1S_0/S^{+\cdot}) > 0.9$–$1.0$ V (sat.c.e.), i.e. with $E_{1/2}(^1S_0/S^{+\cdot}) > E_{1/2}(^1Am_0/Am^{+\cdot})$ (Table 3) are not decolorised on photoexcitation in the presence of A or simultaneously Am and A. These dyes are effective spectral sensitisers of the polymer composition based on Am.A.

The efficiency of the formation of Am_I^+ increases with decrease of the concentration of agents quenching the triplet excitation (for example, O_2), which confirms the idea that triplet-excited dye molecules participate in the sensitisation process.

The oxidation-reduction mechanism of spectral sensitisation has been established by EPR. The first step in the sensitisation process is electron transfer from the amine to the photoexcited sensitiser (Fig.2*a*):

$$^1Am_0 + {}^3S_1 \rightarrow Am^{+\cdot} + S^{-\cdot}. \qquad \text{(XVIII)}$$

The appearance of the EPR spectrum of the radical-cations $Am^{+\cdot}$ (a quartet with intensity ratios of 1 : 2 : 2 : 1) at the instant of the excitation S in the absence of the acceptor component from the layer corresponds to this stage.[120] Further reactions are as follows:

$$S^{-\cdot} + CBr_4 \rightarrow {}^1S_0 + Br^-...CBr_3, \qquad \text{(XIX)}$$

$$Am^{+\cdot} + Br^-...CBr_3 \rightarrow Am_I^+Br^- + CHBr_3. \qquad \text{(XX)}$$

The absence of the EPR spectrum under the conditions of the photoexcitation of S in the presence of only A in the layer and the simultaneous formation of $Am^{+\cdot}$ and radicals formed from $A^{-\cdot}$ as a result of the abstraction of the bromide ion on photoexcitation of S in the presence of Am and A correspond to these stages.[120]

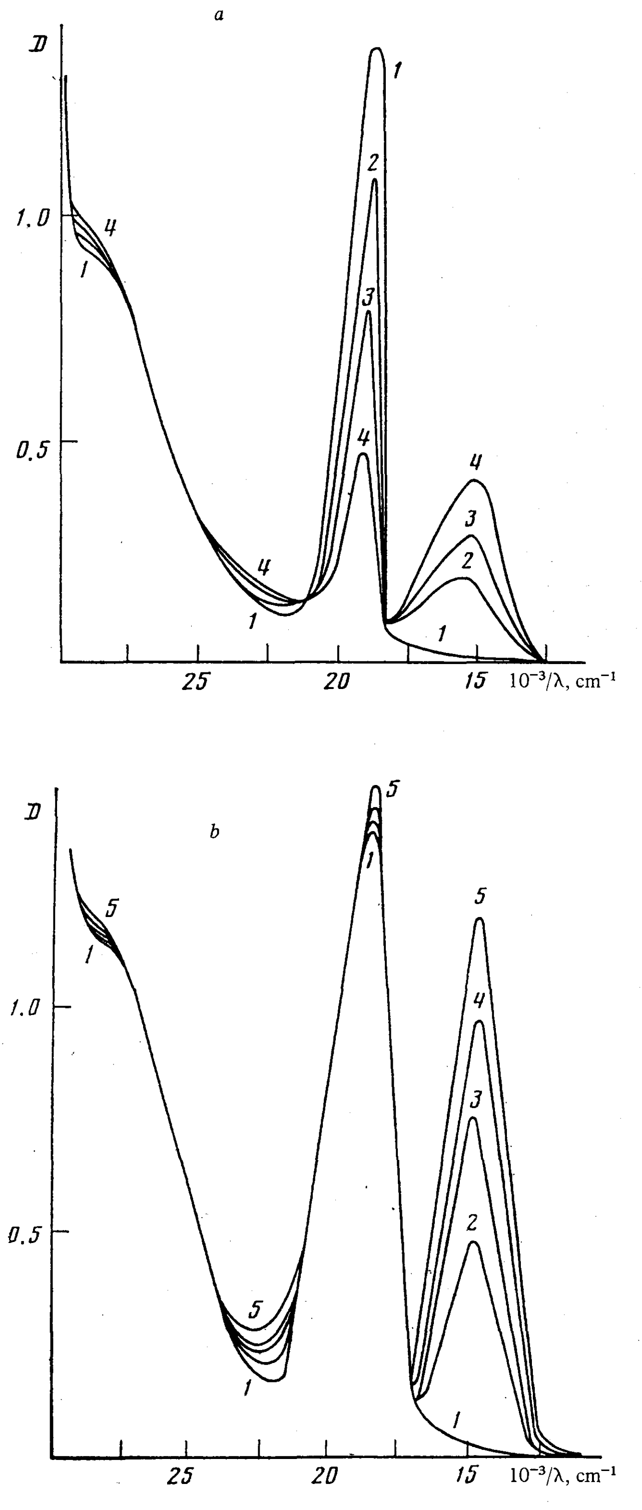


Figure 4. Variation of the optical spectra under the conditions of the photoexcitation of the dye (λ = 531–533 nm, $L_0 = 10^{-3}$ W cm^{-2}) in a composition containing benzyldiphenylamine (0.8 mol dm^{-3}) and CBr_4 (2.3 mol dm^{-3}); [S] = 0.03 ml dm^{-3}; *a*) dye No.7 (Table 3); illumination time (s): *1*) 0 (initial spectrum); *2*) 120; *3*) 240; *4*) 360; *b*) dye No.16 (Table 3); illumination time (s): *1*) 0 (initial spectrum); *2*) 15; *3*) 30; *4*) 45; *5*) 60.[49]

The quantum yield in the formation of the coloured product Am_1^+ via the reactions (XVIII)–(XX) initially increases with increasing concentrations of Am and A:

$$\varphi_{sens} = 0.12[Am][CBr_4]. \qquad (33)$$

Then, after the attainment of the values [Am] = 1 and [A] = 1 mol dm^{-3}, it assumes the constant value $\phi_{sens} = 0.12$.

In conformity with the above scheme (Fig. 2*a*), the cyanine dye participates in reaction (XVIII) at the oxidation-reduction potential $E'_{1/2}(S^{\bar{\cdot}}/{}^3S_1)$, defined by Eqn.(17), while in the secondary reaction (XIX) the reduced sensitiser interacts with the acceptor at the equilibrium potential $E'_{1/2}(S^{\bar{\cdot}}/{}^1S_0)$. The cyanine dyes listed in Table 3 belong to the group for which ${}^3E_{00}$ is related to $E_{1/2}^{ox,\ red}$ by Eqn.(32). Since the value of ${}^3E_{00}$ are unknown for many dyes (Table 3), Eqns.(17) and (32) were used to calculate $E'_{1/2}(S^{\bar{\cdot}}/{}^3S_1)$:

$$eE'_{1/2}(S^{\bar{\cdot}}/{}^3S_1) = eE'_{1/2}({}^1S_0/S^{\dot{+}}) + (\leqslant 0.1) + \Delta G_p^+.$$

The free energy of electron transfer from the Am molecule to ${}^3S_1$ via reaction (XVIII) is (Fig. 2*a*)

$$\Delta G(XVIII) = e[E'_{1/2}({}^1Am_0/Am^{\dot{+}}) - E'_{1/2}(S^{\bar{\cdot}}/{}^3S_1)] = e[E_{1/2}({}^1Am_0/Am^{\dot{+}}) - E_{1/2}({}^1S_0/S^{\dot{+}})] - (\leqslant 0.1), eV.$$

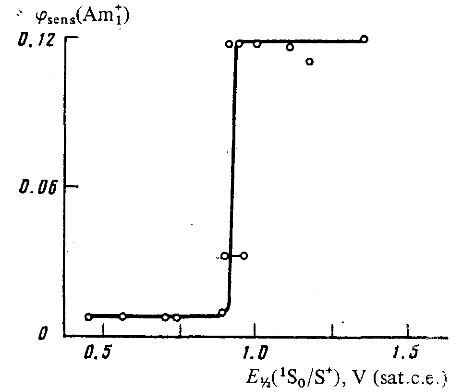


Figure 5. Dependence of the quantum yield ϕ_{sens} for the formation of Am_1^+ on $E_{1/2}({}^1S_0/S^{\dot{+}})$; concentrations of the components (in CPVC): [S] = 10^{-3}, [Am] = 0.8, [CBr_4] = 1.2 mol dm^{-3}.[3], Ch.5; [120]

Fig. 5 illustrates the dependence of ϕ_{sens} on $E_{1/2}({}^1S_0/S^+)$ (Table 3). With increase of $E_{1/2}({}^1S_0/S^{\dot{+}})$, there is a tenfold increase of ϕ_{sens} in the region of $E_{1/2}({}^1S_0/S^{\dot{+}}) = E_{1/2}.({}^1Am_0/Am^{\dot{+}})$ = 0.98 V (Table 3).

Thus the rate of the process is determined by reaction (XVIII) in the formation of Am_1^+ [reactions (XVIII)–(XX)] sensitised by cyanine dyes. The secondary reaction (XIX) does not influence appreciably the quantum yield in the formation of Am_1^+.

The coloured product Am_1^+ is unstable and, as a result of the interaction with CBr_4 and amine molecules, is transformed on heating, with an activation energy of 0.9 eV, into a dye resistant to light and heat[55] and is tentatively assigned to the triphenylmethane series. It has been established[55] that this dye is a sensitiser (autosensitiser) with respect to light active in the region of intrinsic absorption. The mechanism of the autosensitisation apparently consists in the involvement of the photoexcited dye in electron transfer from the donor to the acceptor [reactions (XVIII)–(XX)].[120]

IV. SENSITISATION VIA ENERGY TRANSFER

1. The Role of the CTC as the Triplet Energy Donor

The sensitisation via a mechanism of type (VI) (Section I) has been postulated in a polymer composition based on a CTC between benzylamines (benzyldiphenylamine, dibenzylaniline) and CBr_4.[3,54,57,121,122] According to the existing ideas about the formation of complexes by aromatic amines,[123] their interaction with CBr_4 entails the formation of complexes of at least two types: a complex of the n,σ-type between the nitrogen atom and the acceptor, responsible for the long-wavelength optical absorption (in the range 330–500 nm) of the polymer composition based on $Am.CBr_4$, and the complex of the π,σ-type, which is formed by the aromatic rings of the donor (possibly the excited donor) and the acceptor.

Under the conditions of the photoexcitation of the n,σ-type complex, the quantum yield $\phi(Am_1^+) = 0.12–0.16$ and is independent of [Am] and $[CBr_4]$ [for an optical density $D(Am_1^+) < 1$]. The introduction of a triplet energy acceptor (TEA), namely 1-naphthol, lowers $\phi(Am_1^+)$ and leads to the appearance of the relations[124]

$$\varphi(\mathrm{Am}_1^+) = b[\mathrm{Am}] \text{ and } 1/\varphi[\mathrm{Am}_1^+] = b_1 + b_2/[\mathrm{CBr}_4]. \qquad (34)$$

The appearance of such relations cannot be accounted for on the basis of the idea that a coloured product is formed as a result of the photodissociation of the n,σ-type complex itself, since in this case $\phi(Am_1^+)$ could not correspond to Eqn.(34) and should decrease with increase in the TEA concentration. The reactions leading to the cyclisation of amines, methylphenylamine and diphenylamine (the methylcarbazole and carbazole formation reactions), occurring as a result of triplet energy transfer to amines from triplet energy donors (propiophenone, acetophenone, benzaldehyde, etc.) photoexcited by light with $\lambda = 365$ nm, are well known.[125] It has been established that the effective triplet energy donors for these amines are compounds whose triplet level lies above the position of this level in the amines by 0.06 eV. In the diphenylamine (A), methyldiphenylamine (B), and benzyldiphenylamine series, the optical absorption maxima are at 282, 292, and 296 nm. The positions of the triplet levels in the liquid phase correspond to ${}^3E_{00} = 3.14$ and 3.05 eV for (A) and (B) respectively.[125] It is to be expected that the triplet level in the benzyldiphenylamine molecule is similar to that in compound (B) or is somewhat reduced relative to the latter.

In the light-sensitive system based on $Am.CBr_4$, the influence of TEA can be readily explained by the occurrence of competing reactions on the basis of the idea that, under the conditions of excitation by light with $\lambda = 365$ nm, the complex of the n,σ-type does not dissociate itself but serves as a triplet energy donor for benzyldiphenylamine molecules; the coloured product Am_1^+ is formed as a result of the dissociation of the complex of the π,σ-type:

$$\mathrm{A\cdot CBr_4}(n,\sigma) \xrightarrow{h\nu_{\mathrm{CTC}}\cdot \mathrm{S}_1-T_1} {}^3(\mathrm{Am.CBr_4})_1 - \left[\begin{array}{l} \xrightarrow{\mathrm{Am}} {}^3\mathrm{Am}_1 + \mathrm{Am.CBr_4} \\ \\ \xrightarrow{\mathrm{TEA}} \mathrm{Am.CBr_4} + {}^3\mathrm{TEA}_1 \rightarrow {}^1\mathrm{TEA}_0; \end{array}\right. \qquad \mathrm{(XXI)}$$

$${}^3\mathrm{Am}_1 + \mathrm{CBr_4} \rightarrow {}^3\mathrm{Am}_1.\mathrm{CBr_4}(\pi,\sigma) \rightarrow [\mathrm{Am}^{\dot{+}}\mathrm{Br}^-...\dot{\mathrm{C}}\mathrm{Br}_3] \rightarrow \mathrm{Am}_1^+\mathrm{Br}^- + \mathrm{CHBr_3}.$$

2. Desensitisation

On photoexcitation by light with $\lambda_{inc} = 742 \pm 3$ nm in a composition containing Am and CBr_4, the cyanine dye (Table 3, No.6) is decolorised in accordance with $\phi_{dec} = 0.0052[CBr_4]$ and also sensitises the given composition with respect to red light, ensuring the formation of Am_1^+ and with $\phi_{sens} = 0.0014$ for $[Am] = [CBr_4] = 1$ mol dm^{-3}.[122] The same dye is an effective quenching agent for the photoexcitation of the n,σ-complex $Am.CBr_4$. On photoexcitation of the complex $Am.CBr_4$ by light with $\lambda_{inc} = 365$ nm, this dye is decolorised with the quantum yield $\phi'_{dec} = 0.15$ for $[Am] = [CBr_4] = 1$ mol dm^{-3}.[122] There is no decolorisation under the influence of near UV radiation if the composition contains either no donor or no acceptor component (i.e. the CTC $Am.CBr_4$ is absent). The value of ϕ'_{dec} exceeds by a factor of ~30 that of ϕ_{dec} obtained under the conditions of the photoexcitation of the dye itself. This difference can be due to the fact that by accepting the triplet energy of the CTC, the dye can pass to a second triplet state in which the decolorisation is more effective than in the first.

An effective quenching agent for the excited state of the complex $Am.CBr_4$ is the coloured product Am_1^+. As Am_1^+ accumulates on photoexcitation of the CTC, in the quantum yield in the formation of the coloured product Am_1^+ is given by the following expression when its optical density $D(Am_1^+) \cong 1$ has been reached:

$$\varphi = \frac{0.12k[\mathrm{Am}]}{k[\mathrm{Am}] + k_1[\mathrm{Am}_1^+]} \cong \frac{0.12k[\mathrm{Am}]}{k_1[\mathrm{Am}_1^+]}.$$

This relation can be accounted for by the competition between Am and Am_1^+ [analogously to the behaviour of TEA in reaction (XXI)] for the capture of the energy of the complex ${}^3(Am.CBr_4)_1$ (of the n,σ-type). This desensitisation process determines the photographic characteristics of the light-sensitive polymer layers based on the CTC $Am.CBr_4$.[126]

3. The Sensitisation Effect Associated with the Polymeric State of the CTC

The polymer matrix exerts a sensitising influence in the region of visible light (400–600 nm) on the light-sensitive composition based on the complex $Am.CBr_4$. Indeed, it has been shown on the basis of the complex between benzyldiphenylamine and CBr_4 [127] that the optical spectrum of the complex $Am.CBr_4$ (of the n,σ-type) in the polymer matrix [chlorinated poly(vinyl chloride)—CP VC or polystyrene (PS)] and in the liquid (hexane) has the Gaussian form

$$D(\nu) = D(28{,}2)\exp[-(\Delta\nu_1)^2/\sigma^2] \qquad (35)$$

where $D(28.2)$ is the optical density at the absorption maximum at $\nu_{max} = 28.2 \times 10^3$ cm^{-1}, $\Delta\nu_1 = 28.2 - \nu_1$, and $\nu_1 = 10^{-3}\,\nu$ cm^{-1}.

The hexane $\sigma^2 = 7.0$; in polymer layers σ^2 is independent of the nature of the polymer and amounts to 13.5 in PS and 14.5 in CPVC. Thus, in the liquid phase, the optical spectrum of the complex $Am.CBr_4$ is approximately twice as narrow as in the polymer and does not extend outside the limit of the UV region (the long-wavelength edge corresponds to 400 nm). In the polymer matrix the optical spectrum of the complex extends to 500–600 nm. Apparently this effect occurs because, under the conditions of a limited free volume in the polymer, conformations of the amine in the CTC $Am.CBr_4$, of the type which do not obtain under equilibrium conditions in the liquid, are "frozen". Data have been published,[127] according to which the light sensitivity in the region of the absorption of the complex $Am.CBr_4$ has the following spectral in mind that $E_{1/2}(O_2^{-\cdot}/O_2) = -0.82$ V (sat.c.e.) in acetonitrile:[144]

$$E[^{1,3}(M^{+\cdot}O_2^{-\cdot})_1] = e[E_{1/2}(M/M^{+\cdot}) + 0.82] + \Delta G^{p}_{CTC} + {}^{1,3}Q_e.$$

According to generally accepted ideas concerning the nature of molecular complexes,[145] the wavefunction of the excited oxygen complex $^3(M.O_2)_1$ consists of the set of contributions of the following individual states:

$$\varphi^3(M\cdot O_2)_1 = \alpha_1\varphi_1^3(M^{+\cdot}O_2^{-\cdot})_1 + \alpha_2\varphi_2^3(^3M_1\cdot{}^3O_2) + \alpha_3\varphi_3^3(^1M_1\cdot{}^3O_2) \qquad (37)$$

The wavefunction of the singlet-excited complex $^1(M.O_2)_1$ is given by the set of the following contributions:

$$\varphi^1(M\cdot O_2)_1 = \alpha_1'\varphi_1^1(^1M_0\cdot{}^1O_2) + \alpha_2'\varphi_2^1(M^{+\cdot}O_2^{-\cdot})_1 + \alpha_3'\varphi_3^1(^3M_1\cdot{}^3O_2) \qquad (38)$$

We shall now consider Scheme 1 (Scheme I) when $E(^3M_1) > E[^3M^{+\cdot}O^{-\cdot})_1]$ (Fig. 6*a*). In this case the energetically lowest triplet state is the state with complete charge transfer $^3(M^{+\cdot}O_2^{-\cdot})_1$, which makes the main contribution to the configuration $^3(M.O_2)_1$ [it will be shown below that $\alpha_1 \cong 1$ in Eqn. (37)]. The contribution of other states, determined by the multipliers $(\alpha_2/\alpha_1)^2$ and $(\alpha_3/\alpha_1)^2$, is associated with the relative positions of the energy levels $\Delta E_1 = E(^3M_1) - E[^3(M^{+\cdot}O_2^{-\cdot})_1]$, because $\alpha_2/\alpha_1 = \beta/\Delta E_1$ and $\Delta E_2 = E(^1M_1) - E[^3(M^{+\cdot}O_2^{-\cdot})_1]$, since $\alpha_3/\alpha_1 = \beta/\Delta E_2$. Here

$$\beta = \int \varphi_2^3(^3M_1\cdot{}^3O_2)H\varphi_1^3(M^{+\cdot}O_2^{-\cdot})_1\,d\tau \simeq 0.01-0.1\ \text{eV}$$

is the potential energy of the transferred charge distributed in the electrostatic field of the radical-cation $M^{+\cdot}$.[145] The collision complex $^3(^3M_1.{}^3O_2)$ or the state $^3(^1M_1.{}^3O_2)$ is transformed into $^3(M.O_2)_1$ via the complex formation mechanism (37) with a rate constant $k = \beta/h \cong 2\times10^{12}-2\times10^{13}$ s^{-1} ($h = 4.2\times10^{-15}$ eV s). It is possible to estimate that the contribution to $\phi_3^3(M.O_2)_1$ by the states $^3(M^{+\cdot}O_2^{-\cdot})_1$ is $\geqslant$96% and that by the states $^3(^3M_1.{}^3O_2)$ and $^3(^1M_1.{}^3O_2)$ is $\leqslant$ 4% when $\Delta E_1 \geqq 0.5$ eV. Hence it follows that the formation of the triplet collision complex $^3(^3M_1.{}^3O_2)$ determines the primary electron transfer in the oxidation reaction of the organic compound.

The energetically lowest configuration among the states which contribute to $^1(M.O_2)_1$ [Eqn. (38)] is the collision complex $^1(^1M_0.{}^1O_2)$. The excited complex in the singlet state $^1(^3M_1.{}^3O_2)$, formed on collision of $^3M_1$ and $^3O_2$, is initially transformed, with a rate constant $\beta/h \cong 10^{13}$ s^{-1}, into the configuration with total charge transfer $^1(M^{+\cdot}O^{-\cdot})_1$, which is transformed in its turn into the state $^1(^1M_0.{}^1O_2)$ with a rate constant $\beta_1/h \cong 10^{11}$ s^{-1}, where

$$\beta_1 = \int \varphi_2^1(M^{+\cdot}O_2^{-\cdot})_1 H\varphi_1^1(^1M_0\cdot{}^1O_2)\,d\tau \simeq 10^{-2}\ \text{eV}$$

is the energy of the dipole $M^{+\cdot}O_2^{-\cdot}$ in the potential field of the neutral $^1O_2$ molecule. The dissociation of the states $^1(^1M_0.{}^1O_2:{}^1\Delta_g)$ and $^1(^1M_0.{}^1O_2:{}^1\Sigma_g^+)$ leads to the formation of $^1O_2$ in the forms $^1\Delta_g$ and $^1\Sigma_g^+$. Taking into account the statistical weights of the states with different multiplicities, formed on collision of $^3M_1$ and $^3O_2$ (see Section I), it is to be expected that in the case considered (Scheme 1) 75% of the total number of the triplet-excited molecules $^3M_1$, constituting the state $^3(M^{+\cdot}O_2^{-\cdot})_1$ [see Eqn. (37)], quench the energy in processes involving electron transfer from $^3M_1$ to $^3O_2$, while 25% of the $^3M_1$ participate in the formation of $^1(^3M_1.{}^3O_2)$ [see Eqn. (38)] and lead to the appearance of $^1O_2$. Hence it follows that the compounds satisfying the inequality $E(^3M_1) > E[^{1,3}(M^{+\cdot}O_2^{-\cdot})_1]$ are weak sensitisers of the formation of $^1O_2$ and may be oxidised via the mechanism involving electron transfer to oxygen.

We shall consider Scheme 2 (Section I) (see Fig. 2*b*) when $E(^3M_1) < E[^{1,3}(M^{+\cdot}O_2^{-\cdot})_1]$ and the main contribution to the overall configuration of the triplet-excited state [Eqn. (37)]

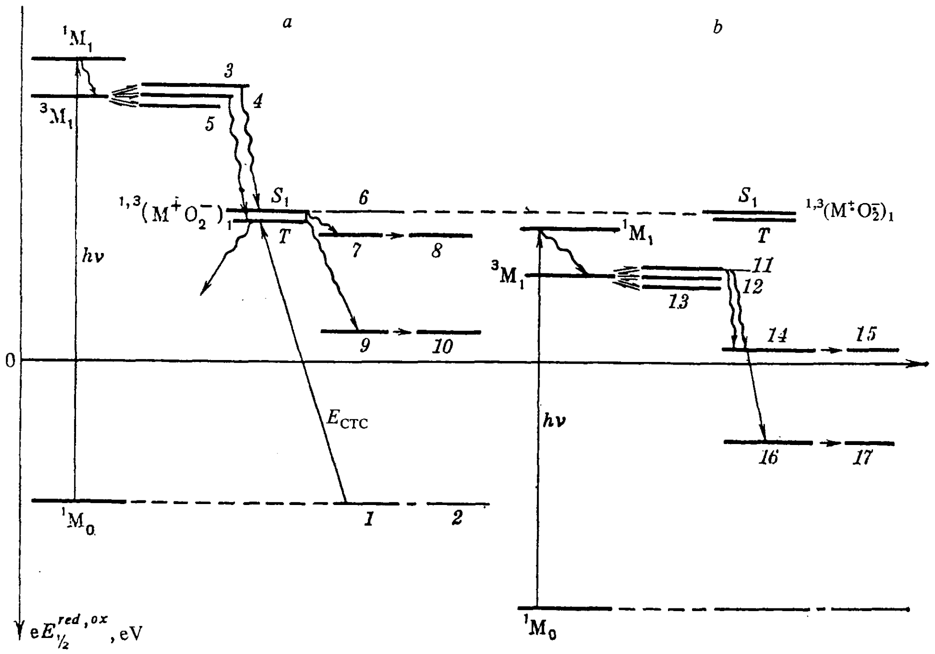


Figure 6. Schematic illustration of the photoprocess with participation of O_2: *a*) $E(^3M_1) > E[^{1,3}(M^{+\cdot}O_2^{-\cdot})_1]$; *b*) $E(^3M_1) < E[^{1,3}(M^{+\cdot}O_2^{-\cdot})_1]$; the molecules M are of different nature and the levels are reckoned from $E(^1M_0) = E_{1/2}(^1M_0/M^{+\cdot})$; the states corresponding to the positions of the levels: *1*) $^3(^1M_0.{}^3O_2)$; *2*) $^3\Sigma_g$; *3*) and *11*) $^1(^3M_1.{}^3O_2)$; *4*) and *12*) $^3(^3M_1.{}^3O_2)$; *5*) and *13*) $^5(^3M_1.{}^3O_2)$, S_1—$^1(M^{+\cdot}O_2^{-\cdot})$, T—$^3(M^{+\cdot}O_2^{-\cdot})$; *6*) $E_{1/2}(O_2^{-\cdot}/O_2)$; *7*), *9*), *14*), and *16*) $^1(^1M_0.{}^1O_2)$; *8*) and *15*) $^1\Sigma_g^+$; *10*) and *17*) $^1\Delta g$.[3], Ch.7.

comes from the state $^3(^3M_1.^3O_2)$. The contribution of the state $^3(M^{\dot{+}}O_2^{\dot{-}})_1$ in Eqn.(37) is determined by the ratio (α_1'/α_2'), where $\alpha_1'/\alpha_2' = \beta_2/\Delta E_3$, $\Delta E_3 = E[^3(M^{\dot{+}}O_2^{\dot{-}})_1] - E(^3M_1)$, and

$$\beta_2=\int \varphi_1^3(M^+O_2^-)_1\ H\varphi_2\cdot{}^3(^3M_1\cdot{}^3O_2)d\tau=10^{-2}\quad \text{eV}\ ^{145}$$

is the energy of the dipole $M^{\dot{+}}O_2^{\dot{-}}$ in the potential field of the neutral molecule $^3O_2$.[145] Hence $(\alpha_1'/\alpha_2')^2 < 2\%$ for $\Delta E_3 > 0.5$ eV and the charge transfer state $^3(M^{\dot{+}}O_2^{\dot{-}})_1$ does not participate directly in the photochemical oxidation process. In this case, which has been considered in detail,[146-148] the efficiency of the transformation of the energy of the triplet-excited molecules into the energy of singlet oxygen reaches 100%.

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The above discussion of the charge transfer reactions with participation of CTC in polymer matrices confirms the validity of the initial postulate that the energy relations of the process are determined mainly by dielectric parameters of the polymer matrix, which functions as a binder for the photoactive components and it is immaterial whether the latter are monomeric or polymeric compounds. This should apparently be manifested in the kinetic characteristics of the process. However, kinetic studies of this kind have so far been clearly insufficient.

One can also conclude that the oxidation-reduction potentials measured in liquid solutions by electrochemical methods and adjusted with respect to the polymer matrix can be usefully employed for the analysis of charge transfer processes in polymers instead of the gas-phase values of the ionisation potential and the electron affinity. Firstly, this is consistent with the essential physicochemical nature of the processes considered and, secondly, it makes it possible to employ the numerous data on the oxidation-reduction potentials of a large number of organic compounds.

It also follows from the above analysis that measurements of the energies of the optical transitions of the donor–acceptor systems in the polymer matrices are necessary, since their comparison with the energies of the analogous transitions in liquid media, where oxidation-reduction potentials are measured, makes it possible to obtain directly the ionisation energies and electron affinities of the molecules in polymer matrices without using the polarisation energies in polymers and in solutions, which are difficult to fix.

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The Surface-modified Carbon Materials for Electrocatalysis

M.R.Tarasevich and V.A.Bogdanovskaya

The principal trends and prospects in studies on the creation of carbon materials with a specified electrocatalytic activity and stability are examined and methods for the surface modification of disperse and compact carbon materials are surveyed. It is shown that charge transport in the electrocatalysis by surface-modified electrodes proceeds via both a mediator mechanism and via direct electron transfer. The electrocatalytic properties of electrodes modified by simple organic complexes, polymers, and biopolymers are discussed and the mechanisms of the acceleration of the electrochemical oxidation of organic substances, the evolution of hydrogen, and the electrochemical reduction of oxygen are analysed.

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I. INTRODUCTION

One of the main tasks in electrochemical science and technology is the creation of new types of electrode materials. For this purpose, vigorous studies have been carried out during the last decade on surface-modified electrodes whose electrochemical and electrocatalytic properties can be altered specifically by varying the surface composition. The "construction" of the surface composition of electrodes is achieved virtually at the molecular level and is therefore extremely promising.

The possibilities in the employment of surface-modified electrodes are wide. They can be used in electrocatalysis, photoelectrocatalysis, and electroanalysis.[1,2] The attachment to the surface of specific electrochemically active compounds makes it possible to create selective electrode materials. The attachment to semiconductors of compounds with a known molecular structure ensures the formation of a surface having the necessary energy level and photosensitive in the specified part of the spectrum.[3] Modification of the surface, especially by polymers, can ensure an increase in the corrosion stability of electrodes and photoelectrodes.[4]

The study of electrodes modified by organometallic complexes makes it possible to obtain information about the influence of molecular conformation on their catalytic and oxidation-reduction properties.

Surface-modified electrodes constitute a convenient system for the elucidation of the mechanism of electron transfer. Studies on electrodes coated by polymers can significantly supplement the available information about the physical chemistry of polymers and biopolymers. Electrodes modified by enzymes are of special interest. The study of enzymes in electrochemical systems opens up a way to the creation of synthetic complexes with a high electrocatalytic activity and selectivity.

Metals, oxides with semiconducting properties, and carbon materials of various types can be used as a basis for the creation of modified electrodes. In the present review attention will be concentrated on electrodes based on carbon materials. According to the authors, this type of surface-modified materials is of greatest interest for practical use.

II. WAYS OF CREATING SURFACE-MODIFIED CARBON MATERIALS

Various methods based on the unique properties of carbon substances are used at the present time to prepare modified carbon materials. Depending on the method of preparation, carbon materials can have compact or disperse forms with the necessary texture of the inner surface. The possibility of the existence of surface carbon atoms in different valence states is responsible for the great variety of the surface oxygen-containing groups. The above properties of carbon materials make it possible to use for the modification of their surfaces of virtually all the known methods for the heterogenisation of catalytically active compounds. They can be divided into three main groups: (1) adsorption methods based on the retention of the modifying agents by physical adsorption forces; (2) chemical attachment with fixation of the catalyst via different groups, including groups specially obtained on the carbon material; (3) deposition of a polymer film with incorporation in the latter of metal ions or an organometallic complex.

1. Crystal-Chemical Properties of Carbon Materials

The physicochemical properties of carbon materials have been fairly completely reviewed in a monograph[5] from the standpoint of their employment in electrochemical systems. We shall deal only with those features of carbon materials which must be taken into account for the successful modification of their surfaces.

(a) *Relation between the electronic structure and the physicochemical properties of carbon materials.* A characteristic feature of carbon materials is the variation of their physicochemical properties as a function of structure for a constant composition. In its turn, the possibility of the formation of a large number of structures is determined by the ability of the carbon atom to exist in different valence states and to form bonds of different types. Depending on the mixing of the *s* and *p* orbitals, the quadrivalent carbon atom can exist in three different hybrid states, a particular structure being characteristic of each. Thus a three-dimensional polymer with tetrahedral bonds between the carbon atoms (sp^3-hybridisation) corresponds to the diamond structure. Graphite, which is a parquet type polymer with sp^2-hybridised carbon atoms, is most often used in electrochemistry. sp-Hybridisation is characteristic of a linear polymer carbon chain. The peripheral carbon atoms in graphite can also exist in the sp-hybrid state. A carbon material with the graphite structure exhibits a marked anisotropy of its physicochemical properties. Thus the electrical conductivities of single crystals in two directions at right angles can differ by three orders of magnitude.

A series of carbon materials having a crystal structure are known: they include graphite and its synthetic analogue (pyrographite), which are characterised by a pronounced anisotropy of their electrical conductivity and other properties. In electrochemistry, crystalline carbon materials are used as a rule to create model electrodes with a small specific surface.

Among the transitional forms of carbon, vitreous carbon, carbon black, and activated carbon are most often used in electrochemical research. Vitreous carbon is characterised by the highest corrosion stability. In terms of their structure, carbon blacks occupy an intermediate position between crystalline graphite and amorphous carbon. Activated charcoals are obtained in the carbonisation and subsequent activation of a wide variety of carbon-containing materials. The texture of the activated charcoal depends on the method of its activation and is characterised by a large set of pores.

The carbon materials used in electrochemical systems must possess a high electrical conductivity, which increases on heat treatment and graphitisation of the transitional forms as a result of the expansion of the graphite-like regions.[6]

(b) *Surface groups in carbon materials.* The bulk-phase and surface properties of carbon materials have been compared.[7] The composition of the surface can be changed during heat treatment in atmospheres of different gases: nitrogen, oxygen, the halogens, ammonia, etc. As a result of such treatment, functional groups capable in many instances of increasing the catalytic activity of the initial material without additional modification are formed on the surface.

Fig.1 presents the most important surface-modifying oxygen-containing groups. They are formed on the surfaces of carbon materials both during synthesis and as a result of the adsorption of oxygen. Among acid oxides, quinonoid, carboxy- and phenolic groups have been detected on carbon blacks and charcoals.[8] Basic oxides are formed under much milder conditions compared with acid oxides. The oxygen is weakly bound to the surface and the identification of basic oxides is difficult.[5] One should also note the possibility of the existence on the surfaces of carbon materials of free radicals, which arise on dissociation of a carbon–carbon bond. An unpaired electron is then liberated and passes to the cyclic carbon system.[9] The adsorption of oxygen entails either a reversible or irreversible decrease of the number of free radicals.

The hydrophobic-hydrophilic properties of carbon materials are closely related to the chemistry of their surfaces. Since the carbon material is apolar, the degree of its oxidation does not affect the adsorption of non-polar compounds. On the other hand, the wettability by water is greater the greater the number on the surface of oxygen-containing groups, which are the primary centres for the adsorption of water.[10] Detailed studies[11,12] established a relation between the nature of the surface oxides and the hydrophilic-hydrophobic properties: surfaces containing basic oxides are more hydrophobic; for low degrees of activation, only macropores and partly mesopores are hydrophobic.

The possibility of the variation within wide limits of the porous structure of carbon materials should also be noted. This is especially important for modification by macromolecules such as enzymes and polymers, because the micropores and some of the mesopores are inaccessible for their adsorption.

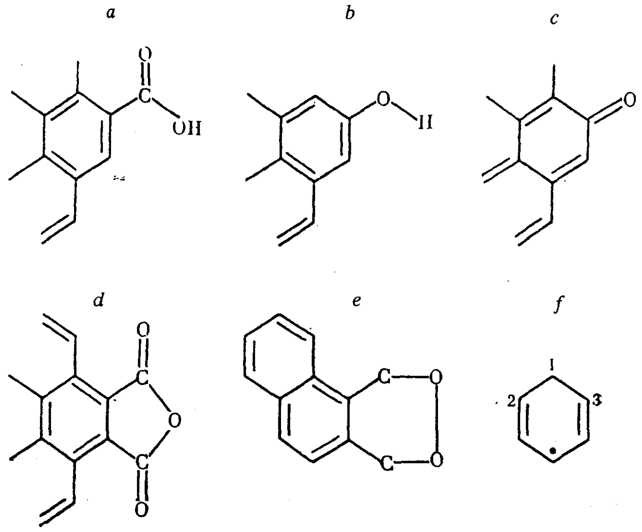


Figure 1. The surface groups of carbon materials: *a*) carboxy-group; *b*) phenolic group; *c*) carbonyl group of the quinone type; *d*) acid carboxy-group; *e*) cyclic peroxy-group; *f*) free σ-radical.

Thus the extensive use of carbon materials for the creation of surface-modified electrodes can be accounted for by the combination of a series of properties such as the presence on their surfaces of a wide variety of groups and free radicals, their high electrical conductivity, and the wide limits within which their porous structures and hydrophobic-hydrophilic properties vary.

2. Attachment by Adsorption

The method of adsorption modification of the surface is best known and simplest. Its principal disadvantage is the gradual desorption of the substance from the surface. The specificity of the adsorption interaction is determined by the type of carbon material and the chemical nature of the substance adsorbed.

Organic materials functioning as ligands for the formation of complexes[13] or metal complexes[14] are immobilised on carbon materials by the adsorption method. The degree of adsorption of organic compounds of this type increases with increase of the number of aromatic rings in the structure. The stronger and irreversible adsorption of N_4-complexes takes place both on polycrystalline pyrographite and on single crystals.[15] According to Zagal et al.[15], the N_4-complexes of iron are adsorbed on the electrode surface in a planar fashion, while tetrasulphonated phthalocyanine complexes of cobalt and iron are disposed on the surface edgewise.

The ability of graphite electrodes to adsorb strongly aromatic molecules has been used[16] to attach the complex $[Ru(NH_3)_5L]^{2+}$, where L is a large aromatic ligand, for example 4-aminomethylpyridine or *N*-(4-picolinyl)benzamide. The complex $[Ru(bipy)_2]_2L^{2+}2(PF_6^-)$, where L is the dianion of 1,5-dihydroxyanthraquinone, has been adsorbed on vitreous carbon.[17] The adsorption of simpler phenanthroline and bipyridyl complexes and also the Salen and corrin complexes of cobalt has been investigated.[18] The strength of their adsorption is low. Macroheterocyclic complexes of cobalt have been adsorbed on carbon materials from their solutions in butanol by evaporating the organic solvent.[19] The complexes are retained on the electrode surface over a wide range of potentials.

The adsorption method for the modification of the surfaces of carbon materials by proteins and enzymes is most widely used in electrochemical measurements. The first studies on the immobilisation of hydrogenase, cytochrome *c*, and laccase on carbon materials already showed that they are strongly adsorbed and that the amount of adsorbed protein is greater the higher the degree of oxidation of the carbon material.[20–22] Peroxidase has been immobilised on carbon black;[23] glucose oxidase and cytochrome b_2 have been adsorbed on vitreous carbon.[24,25] Cytochrome *c* was adsorbed on carbon fibres after the preliminary anodic-cathodic treatment of the surface in the potential range +2.5 to −2.5 V.† This made it possible to observe oxidation-reduction reactions of cytochrome *c*.[26]

In all cases proteins were strongly held on the surface and retained a high catalytic activity. The activity of the enzyme depends on the type of carrier and its specific surface. For example, in the case of laccase immobilised on pyrographite,[2,27] the stationary potential established in an oxygen atmosphere does not exceed 0.9 V; on the other hand, the equilibrium oxygen potential is observed when laccase is adsorbed on carbon black.

An attempt has been made[28,29] to investigate the influence of the nature of carbon sorbents on their capacity with respect to the protein and on the catalytic activity of laccase. The activity of immobilised laccase is influenced by the degree of coverage of the surface by the enzyme, which depends in its turn on the degree of oxidation of the surface of the carbon black or on the porous structure when charcoals are used. The dependence of the activity of the immobilised laccase on the degree of surface coverage in both phenol oxidase and electrochemical reactions passes through a maximum. The greatest capacity with respect to the protein has been noted for charcoals with a large surface area of the mesopores, such as BM-4 and T-39. On the basis of adsorption measurements and porometric data, it has been suggested that macropores and partly mesopores are accessible to the adsorption of protein macromolecules.

However, one should note that, despite the high capacity with respect to the protein, activated charcoals proved to be less convenient electrode materials for the immobilisation of laccase, because in its presence a high anodic potential, inducing the electrochemical corrosion of the charcoal, is established. Carbon blacks exhibit a higher corrosion stability and are more promising for reactions at high anodic potentials with participation of enzymes such as laccase, tyrosinase, and peroxidase.

The favourable and strong adsorption of proteins on carbon materials is determined by the crystal-chemical structure of their surfaces. One of the factors responsible for strong adsorption may be the formation of bonds between the surface groups of the carbon material and the aminoacid residues on the surface of the protein globule. Our studies have shown that the adsorption of many aminoacids and peptides is strong.# Thus glycine and valine cannot be desorbed from the surfaces of carbon materials in the range of their electrochemical stability potentials. Hydrophilic–hydrophobic interactions probably contribute appreciably to the adsorption interaction of the protein with the carbon surface. Their influence on the retention of the nativity of the immobilised proteins has been noted.[30]

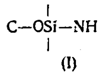
The relation between the isoelectric point of the protein, which determines the surface charge of the protein globule, and the structure of the electrical double layer at the carbon material–electrolyte interface is also noteworthy.

Thus, by virtue of the exceptional properties of carbon materials, strong attachment of the modifying substances, with retention of their high catalytic activity, may be achieved even by adsorption immobilisation.

3. Chemical Modification

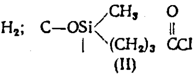
The chemical methods for the modification of the surfaces of carbon materials are based on various organic synthetic reactions.

The most general method for the chemical attachment of modifying agents to the surface involves its preliminary silanisation.[31] Organosilanes, such as the alkylamines (I), the chloroacids (II), and the pyridine derivatives (III) can be used to modify the carbon surface:



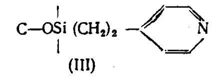
$$\mathrm{C{-}O\overset{|}{\underset{|}{Si}}{-}NH_2};$$

(I)



$$\mathrm{C{-}O\underset{|}{Si}\langle^{CH_3}_{(CH_2)_3\overset{O}{\overset{\|}{C}}Cl}};$$

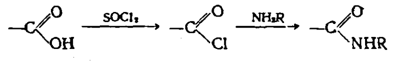
(II)



(III)

The active centres obtained as a result of silanisation are used for the subsequent "grafting" of various electrocatalytically active groups of complexes.[32,33] The ion exchange method,[34] which consists in the formation, for example, of an insoluble compound by reaction between the surface atoms and a ligand, can also be applied to carbon materials.

A very general procedure used for the modification of carbon materials involves reaction with thionyl chloride[34] or acetyl chloride[35] with the intermediate formation of chloride–oxygen compounds:



In order to increase the concentration of the oxygen-containing groups, the carbon material is subjected to preliminary oxidation in air or is treated with an oxygen plasma. The active groups are introduced by the action of amines or alcohols. This method has been used to prepare various modified materials with pyridine and porphyrin ligands.[36–38] The immobilised ligand may then be metallated with formation of electrocatalytically active complexes.

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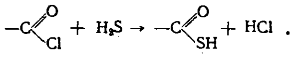
†Here and henceforth, unless otherwise stipulated, the potentials are quoted relative to the hydrogen electrode in the same solution.

#L.R.Aleksandrova, V.N.Andreev, V.A.Bogdanovskaya, and A.Yu.Safronov, Elektrokhimiya, 1987 (in the press).

Amines have been attached[39] to the oxygen-containing groups on carbon materials. This leads to the possibility, in principle, of the subsequent grafting of any functional group.

The intermediate chloride–oxygen compounds on the surfaces of carbon materials can be used for the introduction of various heteroatoms,[40] for example:



$$-C\overset{O}{\underset{Cl}{\lt}} + H_2S \rightarrow -C\overset{O}{\underset{SH}{\lt}} + HCl\ .$$

Another way of creating surface-modified carbon materials involves the use of a surface free from oxides, which can be obtained by the mechanical cleaning of vitreous carbon in an atmosphere of nitrogen or by its treatment with argon plasma.[41] In the presence of vinylpyridine or vinylferrocene, such a surface is modified.

The possibility of attaching the butyl cation or CO_2 to graphite by cathodic treatment in dimethylformamide has been demonstrated.[42]

4. Deposited Films

A special and particularly rapidly developing field concerned with the creation of new electrode materials involves modification by polymers. Here one uses the adsorption, chemical, electrochemical, and radiation attachment methods. The thickness of the polymer films can vary from several to hundreds of nanometers. Depending on the type of reacting or coordinating groups in the polymer film, there is a possibility of its additional modification by metal ions or complexes.

The formation of the polyvinylpyridine complex of copper on various carbon materials by depositing a polymer film from its solution in methanol has been studied in detail.[43] The degree of dispersion of the carbon material influences the activity of the complex, which can be accounted for by the deposition of the polymer in different conformations. The deposition of the polymer film has also been used for the preparation of a surface modified by polystyrene with various functional groups.[44]

The preparation of polyacrylonitrile films on platinum, vitreous carbon, and stainless steel and of polyvinylpyridine films on platinum in a glow discharge at 250 °C has been described.[45–47]

The γ-radiation-induced cross-linking of alkylphenol films is used on metallic electrodes;[48] such cross-linking is also employed for other polymers, which are adsorbed in the monomeric state and are then polymerised.

The methods involving the electrochemical deposition of polymer films, which have many advantages compared with the traditional procedures because they make it possible to eliminate a number of intermedate stages such as the formation of the polymer, its dissolution, etc., have been developing vigorously. In the electrochemical deposition of films, it is possible to regulate the thickness and chemical composition of the resulting coating. On the other hand, electrochemical polymerisation permits the cross-linking of a film already deposited on the electrode.[49]

Polyacrylamide films have been obtained under the conditions of cathodic initiation.[50] Polymer deposits can be obtained electrochemically from solutions containing unsaturated carboxylic acids, certain aldehydes, and alcohols.[51] As a rule, polymer films are deposited electrochemically on metallic electrodes. The uses of polymer electrodes for various purposes, including electrocatalysis and photoprocesses, have been described in a review.[51]

III. ELECTROCHEMICAL PROPERTIES OF THE MODIFIED SURFACES

The study of the properties of surface layers on modified electrodes includes the study of the nature of the bonds between the modifying agents and the surface, the orientation of the modifiers, the degree of surface coverage, the thickness of the layer, the redox reactions of the groups attached to the surface, and the interactions of the species on the surface.

Among the non-electrochemical methods for the investigation of the surface groups of modified electrodes, spectroscopy with optically transparent electrodes,[52] mirror reflection spectroscopy,[53] and also IR and X-ray photoelectron spectroscopy[54,55] should be mentioned. The first two methods are used for the investigation of redox reactions of the attached groups and the last two provide proof that particular stages of the addition reactions have been effected.

The difficulty of measuring the spectra of the modified surfaces *in situ* arises from the necessity to obtain the spectral characteristics of molecules whose number does not exceed that corresponding to a monolayer. Anomalous extinction coefficients have been observed in a series of studies[57–59] on the adsorption of complexes with a conjugated system of π electrons. They all involve the intensification effect due to the roughness of the surface. In the measurement of Raman spectra, this phenomenon has been frequently observed and its possible causes have been considered.[56] In electronic spectroscopy the phenomenon of the anomalous increase of the extinction coefficients was observed for the first time in the adsorption of chlorophyll on an amalgamated gold electrode.[57] Later an analogous phenomenon was noted in the adsorption of tetrasulphonated complexes of cobalt and iron on platinum and pyrographite[58] and of the bipyridyl complexes of ruthenium on SnO_2.[59]

This apparently indicates an extremely strong chemisorption linkage between the modifying group and the electrode surface.

1. Oxidation-Reduction Reactions of the Modifying Complexes

Potentiodynamic and differential pulsed measurements make it possible to investigate the redox reactions of active groups on the surface-modified electrodes and to compare them with the oxidation-reduction properties of the complexes in solution. The possibility of redox reaction of covalently bound groups depends on their orientation on the carbon surface.[60,61] Of the two isomeric 1- and 2-aminoanthraquinones, only the former underwent pronounced redox reactions. It can be oriented parallel to the surface, which ensures the maximum degree of electronic interaction and facilitates electron transfer. Methylaminopropylviologen, attached to the surface via cyanuric chloride, is electrochemically active and stable for a long time.[54] The redox potentials of various ferrocene derivatives attached to graphite differ little from the corresponding values for derivatives in solution in acetonitrile.[40]

Much attention has been devoted to the study of electrodes modified by ruthenium complexes attached to polymers or directly to the carbon surface. In many instances,[13,16] the redox potentials of the adsorbed or chemically attached ruthenium complexes are close to the normal potential of the complex in solution. On formation of metal complexes with polymer films, redox transitions have been observed,[60] whose number depended on whether the metal was coordinated to one or two pyridine rings.

The potentiodynamic curves obtained in the presence of adsorbed phenanthroline complexes of copper[18] show maxima which may be attributed to the Cu^{2+}/Cu^{+} transition on the electrode surface, since the redox potential of the Cu^{2+}/Cu^{+} pair in the corresponding ligand environment is close to the potentials of the redox reactions in solution. As the electrode surface is covered by the complex, a steady increase of the amount of electricity corresponding to the given redox process is observed. The change in the orientation of the complex on the surface is manifested in its adsorption from solutions at different concentrations. A greater order of the adsorption layer, expressed by the fact that the entire complex is reduced and oxidised at similar potentials, is observed in adsorption from dilute solutions. The results of potentiodynamic measurements have shown that redox processes with participation of cobalt and copper complexes proceed under nearly reversible conditions. For complexes of the phenanthroline series, limiting surface coverage approaches the monolayer coverage.

Under the conditions of weak adsorption of the modifying agents,[61] the redox potentials of copper, cobalt, and iron complexes on the pyrographite surface also agree with the corresponding values in solution according to the results of potentiodynamic measurements.

Analysis of all the available data on the oxidation-reduction potentials of various groups attached to carbon carriers leads to the conclusion that their properties in the immobilised state and in solution are similar. This indicates a very high rate of electron transfer from the electrode to the modifying complex.

2. The Influence of the Polymer Coating on the Electrochemical Behaviour of the Carbon Material

The oxidation-reduction reactions of polymer layers on various electrode materials have been described.[62-64] The main results can be summarised as follows. At scanning rates <1 V s^{-1}, the cyclic curves are close to those observed for typical surface reactions. The curves are symmetrical and the current at the maximum is proportional to the rate of application of the potential. These data indicate the absence of transport-dependent limitations. However, at high rates of application of the potential,[65] particularly in the case of relatively thick films,[41,66] a discrepancy between the potentials of the anodic and cathodic maxima is observed. Similar phenomena have been noted on reducing the temperature and on increasing the size of the electrolyte ions.[64]

As a rule, in the case of symmetrical maxima, their parameters differ from those corresponding to equilibrium electronic transitions. Thus the width of the maximum at the level of half the height of the current peak was 0.09 V, which corresponds to a reversible one-electron transition, only in a few cases.[60] Usually this value ranged from 0.15 to 0.54 V. The broadening of the maxima is attributed to repulsive interactions[64] or to a distribution of the given species with respect to the potentials of the redox reaction caused by the existence of electrochemically non-equivalent sites in the polymer film.[3] The asymmetric character of the potentiodynamic $I-E$ curves for polymer coatings can be caused by the slow rearrangement (conformational changes) occurring in the oxidation or reduction of the polymer complex.[66-68] The swelling of the polymers is also possible. Thus significant differences in the behaviour of polymerised vinylferrocene in acetonitrile and water have been noted.[68]

The electrochemical behaviour of polyvinylpyridine (PVP), polycaproamide, and copper polyvinylpyridinate on carbon materials has been studied in detail.[69,70] Fig.2 presents the potentiodynamic curves obtained on a pyrographite electrode with a deposited PVP film. The $I-E$ curves have an analogous form in the presence of a polycaproamide film. It has been noted that the cationic composition of the electrolyte has a significant influence on its polarisation capacity. The relative increase of the polarisation capacity then rises in the sequence Na < K < Ba in the presence of a PVP film and falls in the sequence K > Cs > Ba in the presence of polycaproamide.

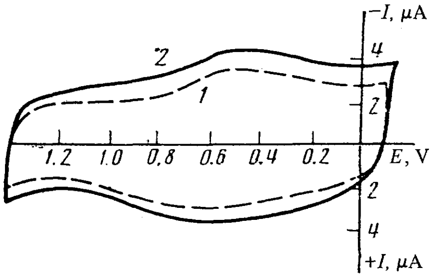


Figure 2. Potentiodynamic $I-E$ curves obtained at a pyrographite electrode (curve *1*) and a pyrographite electrode with a deposited PVP film (curve *2*) for $\nu = 0.05$ V s^{-1} at pH 7.0.[69,70]

When copper ions from an alcoholic solution are introduced into a PVP film, a stable complex is formed, namely Cu-poly-4-vinylpyridine (Cu-P-4VP), which is indicated by the possibility of measuring quasi-stationary potentiodynamic curves in the potential range 1.2–0.0 V.§ The potentiodynamic curves reveal the occurrence of the Cu^{2+}/Cu^{+} redox transition. The successive changes in these curves during the cyclic process suggested the possible conformational rearrangement of the complex in the course of the redox reactions and as a function of time. The stability of the polymer coating is fairly high and is independent of the degree of oxidation of the copper ion. In contrast to this, cobalt complexes decompose on transition of the metal to the bivalent state. The stability of the polymeric copper complex can apparently be explained by the formation of cross-linked structures,[71] as for the ruthenium complexes.[60]

Analysis of the potentiondynamic curves at different rates of application of the potential and with a variable scanning amplitude suggests the presence of at least two types of coordination of copper as a function of the distance between the copper ion and the electrode surface.[43] One of these corresponds to the redox processes at the electrode–polymeric complex interface (type I copper) and the other to the processes occurring in the bulk of the polymer film (type II copper). The redox reactions of type I copper can be described by the following scheme on the basis of the data obtained:

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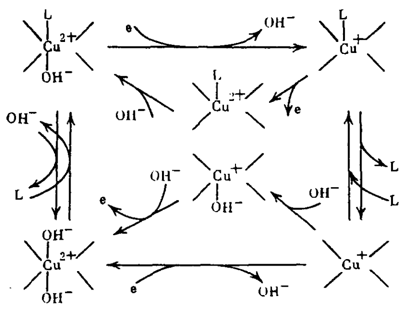
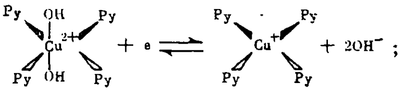
§S.B.Orlov, M.R.Tarasevich, V.A.Bogdanovskaya, and V.S.Pshezhetskii, Elektrokhimiya, 1986, 22, 768.



The surface groups of pyrographite or H_2O can serve as the ligand L. A significant feature of this scheme is the importance of the protonation–deprotonation reaction.

The maximum current for the redox reactions of type II copper is not a linear function of the rate of application of the potential. The following reaction most probably corresponds to this process:



$$\mathrm{Py_4Cu^{2+}(OH)_2} + e \rightleftharpoons \mathrm{Py_4Cu^{+}} + 2OH^- ;$$

Py = pyridine.

It is of interest to note that anodic polarisation at $E = 1.2$ V reduces the height of the anodic and cathodic maxima. The mechanism of this phenomenon can be formulated on the basis of the idea that there are different electrostatic repulsions between neighbouring copper ions in the oxidised and reduced forms, which leads to the contraction and expansion of the ion-containing polymer film in the course of redox reactions and the rate-limiting stage is the relaxation of the polymer chain.

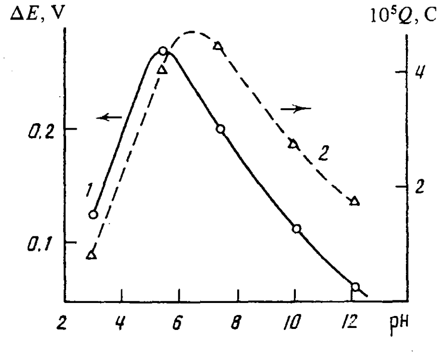


Figure 3. The pH dependence of the shift of the polarisation curve for the electrochemical reduction of oxygen relative to the background curve at $I = 0.03$ mA (curve *1*) and of the overall amount of electricity Q under the I–E curve obtained on pyrographite modified with Cu-P-4VP in the range of potentials 1.2–0.0 V (curve *2*).[43]

Whereas in the absence of copper ions in the polymer coating, the character of the I–E curves is influenced by the electrolyte cations, in the case of the copper-containing PVP the form of the potentiodynamic curves depends on the anionic composition of the electrolyte. Thus the replacement of the PO_4^{3-} ions by Cl^- yields more symmetrical potentiodynamic curves. In conformity with the ideas developed by Shigehara et al.[72], the observed phenomenon can be explained by the facilitation of charge transfer for the polymer layer as a result of migration whose rate is determined by the size of the diffusing counterion (in the given case Cl^-, OH^-, or PO_4^{3-}).

The dependence of the total amount of electricity under the I–E curve on the pH, reflecting the stability of the polymer complex, is illustrated in Fig. 3 (curve *2*). Comparison of this relation with literature data[73,74] shows that tetrapyridinate complexes formed at pH 5–6 are electrochemically active, while the dipyridinate complexes (pH 3–4) are electrochemically inactive. The decrease of the amount of electricity in alkaline solutions (pH > 7) is associated with the formation of copper hydroxide.

The complex character of the kinetic parameters obtained for the electrochemical behaviour of polymer electrodes indicates the necessity to resort to other physicochemical methods for the development of detailed ideas about the mechanism of the redox reactions. One can only note that the redox potentials of a whole series of polymer complexes in solution and in the immobilised state[75,76] change little in the irreversible interaction with the electrode, which indicates the absence of strong ion pairs[77] and shows that the environment of the copper ion on the electrode is close to its environment in aqueous solution.[78,79]

3. The Capacity of Protein Macromolecules for Oxidation-Reduction Reactions in the Immobilised State

The necessity to investigate the electrochemical behaviour of protein macromolecules arises from the prospect of the use of proteins and enzymes in electrocatalysis. The first studies on redox reactions of proteins and enzymes were carried out on mercury electrodes.[2,80,81] However, the interaction of a protein with mercury leads to the partial or complete uncoiling of the protein globule and either the denatured protein or the protein adsorbed on the second layer undergoes the oxidation-reduction reactions.[2] Furthermore, in their interaction with mercury, sulphur-containing proteins form compounds of the type $(HgS)_2$ and the potentiodynamic curves reflect their redox reactions.[81] It has been established that the potential of the oxidation-reduction reactions of these compounds is identical with the redox potential of the transition $HgS \rightleftharpoons Hg^{2+} + S^{2-}$ observed for a sulphur-containing aminoacid—cysteine.

In this respect, carbon materials are superior to mercury. In the first place, it has been shown[2,14,27] that proteins and enzymes retain their catalytic activity after adsorption on the carbon carrier and are therefore not denatured. Some decrease of activity may be explained by the restriction of mobility on formation of bonds between the surface groups of the protein globule and the corresponding groups of the sorbent.

The redox reactions of cytochrome *c* on carbon fibres have been described[26,82] and it has been shown that cytochrome *c* is oxidised and reduced almost reversibly. Our investigations¶ on a pyrographite electrode subjected to preliminary anodic-cathodic activation in the potential range 2.0 to −2.0 V showed that cytochrome *c* is oxidised and reduced at potentials close to the oxidation-reduction potential of the

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¶V.A.Bogdanovskaya, A.M.Kuznetsov, M.R.Tarasevich, E.D.German, and E.F.Gavrilova, Elektrokhimiya, 1987 (in the press).

protein. The rate of reduction of the protein in the temperature range 5–20 °C is independent of temperature. Calculation carried out on the assumption that one electron is consumed on the reduction of the active centre of cytochrome *c* showed that the surface coverage of pyrographite by the protein does not exceed a monolayer.

It has been noted[83] that, in electrochemical systems with electrodes made of carbon materials, the redox reactions of the active centre may be accompanied by the oxidation of certain aminoacids, for example, tyrosine. However, this hypothesis is unlikely, because the oxidation of aminoacids at a potential of +0.66 V relative to the silver, silver chloride electrode is hardly feasible; it is contradicted by data on the electrochemical oxidation of aminoacids.[84–86]

The electrochemical reactions of enzymes on carbon materials have been investigated[81,87,88] and it has been shown[81] that peroxidase does not undergo redox reactions in the experimental potential range. On the other hand, when peroxidase is denatured, the haem liberated gives rise to almost reversible maxima. It has been stated that laccase is reduced on carbon black at a potential of 0.75 V.[87] The possibility of the oxidation-reduction of glucose oxidase has been noted,[88] but systematic studies of the oxidation-reduction properties of enzymes have not so far been carried out. One of the causes of this may be the high redox potentials of enzymes, which require the use of special electrode materials stable at these potentials. Mercury electrodes dissolve at fairly low potentials and carbon materials are corroded at potentials more positive than 1.0 V.

IV. CHARGE AND MATERIAL TRANSFER IN THE SURFACE LAYER

An adequate description of the mechanism of charge and material transfer in the surface layer at the interface between the conducting support and the bulk of the electrolyte is the main fundamental task in the problem of modified electrodes. Only on the basis of data for the mechanism and kinetics of transport stages can one estimate the possible limits of the acceleration of electrochemical reactions and optimise the electrocatalytic effect.

The main trends in the study of transport processes are the calculation of the rate of transfer of charged species, the search for phenomenological models for the representation of experimental data, and direct experimental investigation of the electron (charge) transfer stage.

In the case of monolayer coverage, the transport stages as such are absent and the mechanism of the electron transfer between the metal and the substrate is determined by the character of the electronic interaction of the metal, the catalytically active group, and the substrate. For a distributed catalytically active layer, the redox reaction of the substrate can occur throughout its bulk and electron transport is achieved via jump or mediator mechanisms, with the simultaneous diffusion of counterions. Depending on the morphology of the active film, account must be taken also of the diffusion of the substrate in the pores or through the film (Fig. 4).

As shown above, the redox potentials of compounds immobilised on electrodes differ little from the corresponding values in solution, which indicates rapid electron transfer in those cases where a direct electronic interaction of the active group and the support is established as a result of the overlap of the corresponding electron orbitals. In a series of studies,[3,67,89] the potentiodynamic I–E curves for surface-modified electrodes were examined quantitatively taking into account the interaction of neutral and charged surface groups, the heterogeneous properties of the surface, and the effect associated with the rearrangement of the surface layer as a function of time. The dependences of the potential of the maximum and of the current at the maximum on the rate of scanning of the potential are described by fairly complex equations. By means of numerical computer calculations, it is possible to "adjust" the shape of the calculated I–E curve to agree fairly well with the experimental curve. However, in view of the large number of initial assumptions, this can hardly serve as proof of their validity.

The general relations governing electron jumps via the tunnel mechanism† have been examined in a number of studies.[90–93] The influence of the degree of interaction of the adsorbate with the surface on the tunnel electron transfer in the electrode/adsorbate/redox pair system has been analysed. For a very strong interaction, a volcano-like dependence of the exchange current on the electron work function of the metal has been predicted.[92] The height of the potential barrier on the residence time of the electron in the intermediate state determines whether electron transfer is of the two-channel type or the multichannel type.

Tunnel electron transfer takes place in the redox reaction of immobilised ferrocene[94] at a distance of 8 Å from the surface of the electrode. The temperature variation of the rate of reaction obeys the Arrhenius equation. The change in the rate of reaction by two orders of magnitude on passing

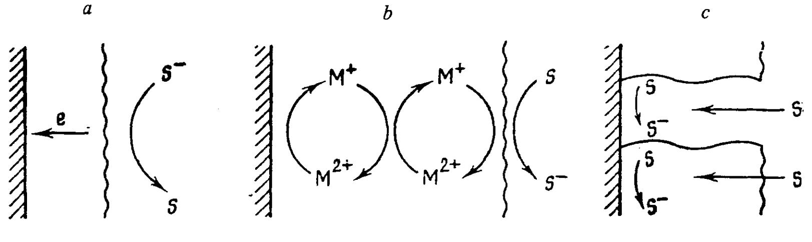

Figure 4. Methods of carrying out the redox reactions of the substrate S on surface-modified electrodes: *a*) injection of charge into the film; *b*) mediator transport (M = mediator); *c*) diffusion through the film or in the pores.[5]

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† Since the number of studies devoted to tunnel transport is small, we shall employ the available data regardless of the type of conducting support.

from sulpholan to acetonitrile is associated with the change of the activation energy from 44 to 34 kJ mol^{-1}. Using the elastic tunnelling model, the authors[94] begin with the fact that the overall activation energy for the electronic transition in the given system is made up of the energies of the reorganisation of the solvent and of the change in the bond lengths. However, this assumption is arbitrary, since the first process is adiabatic and the other is not.

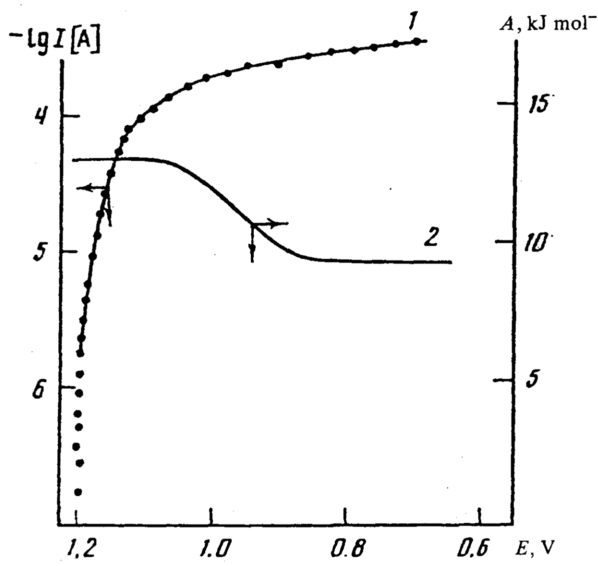

Figure 5. Dependence of the rate of electrochemical reduction of oxygen (curve *1*) and the activation energy for this reaction (curve *2*) on the potential of a carbon black electrode with immobilised laccase.[97]

Tunnel electron transfer has been examined as the transport stage for carbon electrodes modified by enzymes.[95–97] The dependence of the rate of the cathodic reduction of oxygen on a carbon black containing laccase on the thickness of the lipid layer between the protein globule and the support has been investigated.[95] For a thickness of the lipid layer in excess of 20 Å, the rate of reaction falls sharply, which is caused, according to the authors, by the decrease of the effective tunnel electron transfer. The estimates of the possible distance over which tunnel electron transfer takes place[95,97] were based on the hypothesis of rapid electron transfer between the electrode and the active centre and that the rate of the process is limited by the rate of the enzyme reaction.

Detailed studies of the kinetic characteristics and of the temperature variation of the rate of reaction[97] deepened the existing ideas about the mechanism of the bioelectrocatalytic oxygen reduction reaction. In the region of relatively low polarisations, the rate of the electrochemical reduction of oxygen is limited by the rate of the electron transfer stage and is described by the Tafel relation between the current and the potential (Fig.5). In the region of the limiting current, the process is controlled by the stage characteristic of enzyme catalysis.

In the region of low polarisations, the activation energy A is low and the acceleration of the reaction is to a large extent caused by the change in the pre-exponential factor ν in the equation

$$i=\nu\exp(-A/kT) \ .$$

Application of modern quantum theory[98] permitted the conclusion that a collectivised state of the adsorbent–adsorbate system arises in the immobilised laccase–carbon electrode system. The electron density is not localised on the active centre of the enzyme, because its interaction with the solvent is weak. The oxygen electrochemical reduction current is

$$i\cong\int d\varepsilon\rho_a(\varepsilon)f(\varepsilon)W(\varepsilon)\sim\rho_a(\varepsilon^*)f(\varepsilon^*)W(\varepsilon^*) \ ,$$

where $f(\varepsilon)$ is the Fermi function of the distribution of the energy of the electrons, $W(\varepsilon)$ the probability of electron transfer from the level ε on the active centre to the substrate molecule, $\rho_a(\varepsilon)$ the density of electronic states associated with the active centre, and ε^* the energy for which the contribution to the total current is a maximum. Since the active centre of the enzyme is at a distance of ~10 Å from the electrode their potentials are different. The dependence of the pre-exponential factor on the potential is then determined by the influence of the latter on the energy of the electronic level of the active centre of laccase.

In the study of charge transfer# in multilayer (including polymer) electrodes containing active centres, three possible mechanisms are taken into account: electron jumps, exchange of electrons between the active centres, and the diffusion of counterions. It is usually assumed that the electron transfer process through the polymer is analogous to diffusion:[99]

$$D_{\text{exp}}=D_0+\pi k\delta^2c/4 \ , \qquad (1)$$

where D_0 characterises the actual contribution of diffusion, k is the rate constant for electron exchange between the redox centres in the polymer layer, c the concentration of the species reduced at the electrode, and δ the distance over which the electron is transferred.

In order to elucidate the mechanism of electron transfer, one investigates the influence on the latter of temperature, the type of solvent, the nature of the electrolyte, the degree of cross-linking of the polymer, and the concentration of charges. The determination of the apparent diffusion coefficient D_{exp} for a polymer of the nafion type on a pyrographite electrode[101] showed that the charge transfer mechanism depends on the type of cation incorporated. Fig.6 illustrates schematically the dependence of D_{exp} on the concentration of active groups for polymers of two types differing in the strength of attachment of the active centres. An example of the system of type (*a*) is provided by a copolymer containing ruthenium and osmium ions;[102] the system (*b*) obtains for a polymer containing the Ru(bipy)$_3^{3+/2+}$ ions.[101] Section *2* is described in both cases by Eqn.(1) presented above. In region *3*, the rate of transfer is determined by the mobility of the polymer lattice or polymer chains. In region *1* (*a*), ions are separated by a distance greater than the characteristic diffusion distance and the rate of transfer diminishes. Region 1 (*b*) corresponds to simple diffusion of ions. Comparison of the diffusion coefficient and of the rate of quenching of the luminescence of Ru(bipy)$_3^{2+}$ [103] leads to the conclusion that the slow stage is the movement of counterions. The diffusion mechanism is

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#The electronic properties of the polymers themselves, including those which have been doped electrochemically, have been examined in a review[100] and a monograph.[101]

most important for thick films and when there is a significant difference between the potentials of the substrate and the attached mediator.

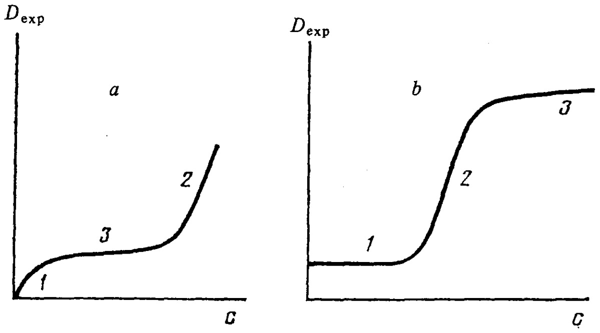

Figure 6. Schematic illustration of the dependence of D_{exp} on the concentration of active groups for polymers with chemically attached (*a*) and electrostatically bound (*b*) ions; for the characteristics of sections *1–3*, see text.[101]

A series of experimental facts outside the framework of the ideas formulated above have been described in the literature. Thus it has been observed[104] that, when copper ions are incorporated in polyphenol oxidase films at Cu^{2+} concentrations above the critical value, there is an avalanche-like increase of the rate of electron transfer. A phenomenon, previously unknown, involving an increase in the polarisation capacity in the pyrographite–polymer–electrolyte system has been described.[69,70] The magnitude of the effect depends on the nature of the cation and decreases with decrease of the radius of the hydrated cation. It has been suggested that this is associated with the shielding by the cationic charge of the free electrons of the support, entering the polymer layer, and not with the doping of the polymer by electrolyte cations.

The ideas about the mechanism of charge transport are used to solve two main problems: the analysis and quantitative description of the redox reactions in the surface layer and the estimation of electrocatalytic effects which can be attained using electrodes of the type considered. In the interpretation of the form of the *I–E* curves, one begins with the idea of slow heterogeneous electron transfer and data on the kinetics of the reorganisation of the film and the interaction within the film.[67,105]

An attempt has been made to estimate the efficiency of electrocatalysis on the surfaces of modified electrodes compared with homogeneous catalysis. It has been shown[89] that, for the same activation energy, homogeneous catalysis is more effective than electrocatalysis under conditions where the concentration of the active centres corresponds to monolayer coverage. Bearing in mind the influence of binary and ternary collisions and also the electrostatic work of the double layer and the reflection layer, large effects cannot be expected in the case of an outer-sphere mechanism of electrocatalysis. This is confirmed by calculations for a surface-modified disc electrode.[89]

In estimating the electrocatalysis effect for electrodes with a distributed active layer, one must take into account the rate of transfer of both electrons and of the substrate to the active centre. Various instances of electrocatalysis on polymer electrodes with redox centres have been investigated theoretically and experimentally.[106,107] If the electron transfer stage is rapid (on the electrochemical scale), then polymer or multilayer coatings are useful when the transport stage is relatively slow and the films are readily permeable. However, this conclusion is hardly valid if the polymer exhibits electronic conductivity[108] or when a conducting filler, for example, carbon particles, has been introduced into the film.

The stationary diffusion equations for a disc electrode coated by an electrochemically active polymer film have been examined.[89,109] In this case the thickness of the diffusion layer δ is replaced by the quantity $\delta' = l + (D_f/D_s)_\delta$, where D_f and D_s are the diffusion coefficients in the film and in the free solution. If the rate of diffusion in solution is much smaller than in the film ($D_s/\delta \ll D_f/\delta$), then the usual voltage–current curves are obtained. For the opposite relation, the system becomes more reversible than on the "clean" electrode. However, this is manifested by the approach of the half-wave potential to the reversible value and not by the increase of the overall current.

V. NON-ELECTROCATALYTIC REACTIONS ON MODIFIED ELECTRODES

In simple oxidation-reduction reactions unaccompanied by a redistribution of the bonds or strong coordination of the molecules, the modifying groups serve as mediators in electron transfer processes. The rates of reaction of this type are independent of the nature of the electrode material after the application of corrections for changes in the structure of the double layer, but data for their kinetics yield much information necessary for the understanding of the mechanisms of electrocatalytic reactions.

Three types of non-catalytic reactions on surface-modified electrodes are possible. If the substance is oxidised more readily than the mediator modifying the surface and the film of the modifying agent is poorly permeable to the reacting substance, the process proceeds on the outer boundary at the redox potential of the mediator. If the redox potentials of the mediator and the reactant are equal, the reaction proceeds in the same way as on an unmodified surface. The third case, where the mediator is oxidised more readily than the substrate and its transfer becomes dominant, is of greater interest. This mechanism has in fact been observed.[110] The complex $K_4Mo(CN)_8$, introduced into a PVP film on pyrographite, can act both as an oxidant and as a reductant. The processes occurring in the system are illustrated schematically in Fig.7. The redox potential of the $Mo(CN)_8^{4-}/Mo(CN)_8^{3-}$ transition for the complex incorporated in the film is +0.52 V, while for the Fe^{2+}/Fe^{3+} system it is +0.49 V. The closeness of these redox potentials makes it possible to accelerate both the oxidation of Fe^{2+} and the reduction of Fe^{3+}. The above hypotheses are confirmed by the curves (Fig.7) obtained for electrodes of three types: unmodified, modified with PVP, and modified with PVP containing the complex $K_4Mo(CN)_8$.

The second cause of the interest in non-catalytic reactions on modified electrodes is the possibility of investigating the redox reactions of proteins on such electrodes. Studies of the electrochemical reactions of their active centres are of special interest. In such systems, the modifying agents play the role of mediators and at the same time serve as enzyme substrates, which makes it possible to achieve the redox transformations of the active centres. As a rule the redox reactions of proteins are investigated on modified metallic electrodes. Thus the immobilisation of methyl- or benzyl-viologen on gold makes it possible to carry out the oxidation-reduction reactions of myoglobin,[111] while the immobilisation of polyvinylviologen permits the reduction of cytochrome *c*.[112] Cytochrome *c* can be oxidised and reduced electrochemically on gold and platinum electrodes with adsorbed 4,4'-bipyridyl.[113]

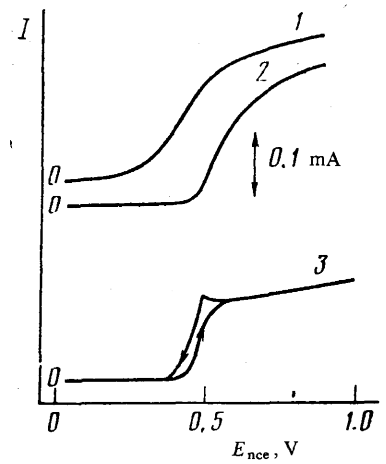

Figure 7. Polarisation curves for the oxidation of Fe^{2+} (at a concentration of 4 mM) at pH 1.5 and $v = 0.0075$ V s^{-1} at a rotating pyrographite electrode (curve *1*) and a pyrographite electrode modified with PVP (curve *2*) and the $PVP-Mo(CN)_8^{4-}$ complex (curve *3*).[110]

On a carbon surface, the redox reactions of proteins have been observed both after the modification of the electrode and after the preliminary electrochemical treatment of the surface. Cytochrome *c* is reduced on pyrographite modified by polymeric methylviologen[114] and peroxidase, glucose oxidase, and xanthine oxidase, as well as certain other enzymes are reduced on vitreous carbon.[115,116] The electrochemical reactions of laccase occur in the presence of a whole series of modifying agents and the positions of the potential maxima depend on their nature. On modification of 2,9-dimethylphenanthroline, the maximum is at 0.64 V, while on modification with 4,4'-bipyridyl it is at +0.74 V (n.h.e.).[115,117]

The anodic-cathodic treatment of the surface can result in the appearance of a large number of oxygen-containing groups which function as modifying agents. The redox reactions of cytochrome *c* have been observed on electrochemically treated carbon materials.[26] It is most likely that oxygen-containing groups, including quinone-hydroquinone groups, effect the oxidation-reduction reactions of the active centres of the proteins via the mediator mechanism.

VI. THE MECHANISMS OF ELECTROCATALYTIC REACTIONS

By virtue of the possibility of the specific creation of an active layer, surface-modified electrodes have been finding increasing application in a whole series of electrocatalytic reactions, because they exhibit an increased selectivity and a high catalytic activity.

1. The Activation of Organic Molecules

The oxidation reactions of organic molecules proceed as a rule at high anodic potentials on platinum group metal electrodes. The use of surface-modified electrodes permits in many cases the elimination of noble metals or it is even possible to achieve reactions which cannot occur on other electrodes.

Using modified pyrographite, sulphoxide has been synthesised[118] and anisole and toluene have been chlorinated.[119] The yield of the target products, namely carbinol and pinacol, on a graphite electrode modified with amine depended on the nature of the surface oxides.[119] In the presence of basic oxides, pinacol was synthesised preferentially, while on a surface coated with acid groups, carbinol was the main product. Presumably the strength of the bond between the modifying amine and the electrode surface plays an important role.

Data have been published[55] on the acceleration of the oxidation of ascorbic acid on pyrographite electrodes with chemically bound benzidine. It is noteworthy that preliminary treatment with plasma leads to an increase of the true surface area of the pyrographite electrode and the true acceleration effect is therefore not unduly great. Graphite electrodes modified with vinylferrocene are the most effective in this reaction.[120] The electrocatalytic current is limited by the rate of diffusion of ascorbic acid in the polymer film. The graphite electrode modified with quinone[54] accelerates the electrochemical oxidation of NADH to NAD^+. The oxidation of NADH is accelerated to an even greater extent in the presence of polymer films of dopamine (DP), phenazine methanesulphonate (PPMS), and phenazine ethanesulphonate (PPES).[121] [The latter two films are not mentioned in Ref.121 (Ed.of Translation)]. Data concerning the acceleration of the reaction in the presence of the above compounds are compared in the Table. It is noteworthy that the half-wave potentials ($E_{1/2}$) and current maxima (E^*) for the oxidation of NADH (see Table) are remote from the redox potential of the $NADH/NAD^+$ pair, which is −0.56 V (s.c.e.).

The half-wave potentials ($E_{1/2}$) and the potentials at the maximum (E^*) for the oxidation of NADH on electrodes modified by different compounds at pH 7.0.[121]

Type of modifying agent	Quinone	PD	PPMS	PPES
$E_{1/2}$, V	+0.16	+0.12	−0.16	−0.21
E^*, V	+0.26	+0.21	−0.05	−0.10

The high catalytic activity of pyrographite modified with tetrasulphonated water-soluble phthalocyanine complexes of iron and cobalt in the oxidation of certain organic molecules has been noted.[1,2] The phthalocyanine complex of cobalt accelerates the oxidation of cysteine to cystine. In both acid and alkaline solutions, the slope of the Tafel curve is close to $2 \times 2.3RT/F$. In the region pH < 8.5, we have $\partial \lg i / \partial \text{pH} \cong 1$, whereas at higher pH the corresponding function is close to zero. These kinetic parameters correspond to the following possible reaction mechanisms:

$$R{-}SH \rightleftharpoons RS^- + H^+ ,$$
$$RS^- \rightarrow RS^{\cdot} + e ,$$
$$2RS^{\cdot} \rightarrow R{-}S{-}S{-}R .$$

The use of carbon electrodes modified by enzymes for the oxidation of various organic substrates has been examined fairly fully.[96] Enzymes of the oxidase class—cytochrome b_2, peroxidase, glucose oxidase, xanthine oxidase, and galactose oxidase—effect the reaction of their substrates in the immobilised state on the electrode. Two reactions take place consecutively on two-enzyme electrodes based on glucose oxidase and peroxidase:

$$\text{glucose} + O_2 \xrightarrow{\text{glucose oxidase}} \delta\text{-gluconolactone} + H_2O_2;$$

$$H_2O_2 + 2Fe(CN)_6^{4-} + 2H^+ \xrightarrow{\text{peroxidase}} 2Fe(CN)_6^{3-} + 2H_2O.$$

Xanthine oxidase or uricase may be used in two-enzyme electrodes. Analysis of the experimental data shows that the rate-limiting stage in the overall process is the first reaction,[123] i.e. the oxidation of glucose, hypoxanthine, or uric acid. The efficiency of such electrodes is extremely low and the creation of electrochemical sensors for the detection of various substrates is a more realistic application of such devices.

Immobilised enzymes belonging to the class of dehydrogenases can be used for the oxidation of organic substrates. As a rule, the regeneration of coenzymes, which can be achieved with the aid of enzymes, is essential for their functioning. NAD was regenerated in the presence of alcohol dehydrogenase and lactate dehydrogenase.[124] However, such a system is unduly complex and its employment is hardly promising.

Enzyme electrodes based on hydrolases immobilised on a graphite paste electrode or vitreous carbon have been examined.[96] The enzymes are retained in the vicinity of the electrode surface with the aid of membranes. The operation of such electrodes is based on the fact that the hydrolase, for example, cholinesterase, effects the reaction which is typical for such enzymes, involving the cleavage of a covalent bond in the substrate, while the product of the enzyme reaction participates in the electrochemical reaction. Catechol mono-orthophosphate, indoxyl acetate, and other substrates have been oxidised in this way.[96]

The mechanisms of the electrochemical oxidation reactions on electrodes whose surfaces have been modified by enzymes have been studied little. As a rule, the authors confine themselves to comparing the enzyme and electrocatalytic activities and to the calculation of the Michaelis constant. On the basis of these data, it is concluded that the nature of the rate-limiting stage is kinetic or diffusional.[96] Systems in which the electrochemical and enzyme reactions are coupled with the aid of mediators have been studied in greater detail. In essence, such systems do not belong to the class of surface-modified electrodes, because the enzyme immobilised on the electrode effects the enzyme reaction and the acceleration of the electrode reaction is due to the overall effect of all the processing occurring in the system.

Our studies on the oxidation of model compounds derived from lignin (hydroquinone, guaiacol, syringol, and veratrole) on a carbon black electrode modified with laccase demonstrated the possibility, in principle, of the oxidation of these compounds.§ According to the results of chromatographic analysis, the products of electrochemical oxidation on the unmodified and laccase-modified carbon black electrodes are different.

2. Acceleration of the Hydrogen Evolution Reaction

Carbon materials modified by titanium compounds, namely $C{-}OTiCl(OC_2H_5)_2$ or $C{-}OTiCl(OH)_2$, have been used to activate the hydrogen reaction.[39] The potentiodynamic curves obtained for such electrodes show an anodic maximum in the potential range between −0.3 and −0.4 V after cathodic polarisation to $E = -0.6$ V. After prolonged cycling, the shape of the curves does not change, which indicates fairly strong binding of the titanium compounds. With increase of the amount of attached compound, the rate of hydrogen evolution also increases. The reaction on the unmodified carbon material may be represented as follows:

$$2Ti^{IV} \xrightarrow{2e} 2Ti^{III} \xrightarrow{2H^+} 2Ti^{IV} + H_2.$$

The reverse reaction involving the anodic oxidation of molecular hydrogen is not accelerated in the given system, which agrees with the results of a study[125] where it was shown that carbon modified by titanium compounds does not catalyse the hydrogenation of aromatic compounds by molecular hydrogen.

Carbon materials with an immobilised hydrogenase have been used[2,126] to accelerate the electrochemical oxidation of hydrogen. Methylviologen (MV) was used as the mediator in this system. The redox potential of the MV^{2+}/MV^+ pair is +0.011 V, i.e. is extremely close to the equilibrium hydrogen potential. The overall result of the set of reactions is the oxidation of molecular hydrogen:

$$E + H_2 \rightleftharpoons EH_2,$$

$$EH_2 \rightleftharpoons EH^- + H^+,$$

$$EH^- + MV^{2+} \rightleftharpoons MV^{\dot{+}} + E + H^+ + e,$$

$$MV^{\dot{+}} \rightarrow MV^{2+} + e,$$

$$E = \text{enzyme}.$$

The activity of the immobilised hydrogenase and the rate of reaction are higher the greater the amount of enzyme adsorbed on the carbon black, which may be due to the fact that at low coverages there is a strong interaction of the enzyme with the carrier leading to partial denaturation of the protein. With increase of the surface coverage, the interaction of the enzyme with the support weakens, the molecules are oriented in the most favourable manner, and the activity of the enzyme approaches that of the native form.

Kinetic studies have been made of the hydrogen reaction under the conditions of the direct electron transfer from the active centre of the enzyme to the electrode.[127] However, analysis of the electrochemical data refers to the range of potentials where the process is concentration dependent and the observed stoichiometric number yields no information about the mechanism of the kinetic stage.

The use of electrodes modified by polymers and complexes based on them for the activation of the hydrogen reaction has not as yet been described.

3. The Oxygen Reaction

The majority of studies of the use of surface-modified electrodes in electrocatalysis are associated with the reduction of molecular oxygen. At the present time several ways of making modified electrodes for this purpose have been developed: the binding of quinones and phenanthroline and bipyridyl complexes and N_4-complexes, the "assembly" on the electrode surface of polymer systems of various types, and finally the modification of the electrode surfaces by enzymes.

Fig.8 presents the group of quinones which have been used to accelerate the reduction of oxygen in neutral electrolytes.[39] When the quinones R^3 and R^4 with asymmetric substituents are adsorbed, steric hindrance obtains, and they exhibit only

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§ V.A.Bogdanovskaya, M.R.Tarasevich, and V.G.Vorob'ev, in "Novosti Elektrokhimii Organicheskikh Soedinenii" (New Aspects of the Electrochemistry of Organic Compounds), Moscow—Lvov, 1986, p.65.

a weak catalytic activity. On the other hand, the molecules of R^2 and R^5, which each contain two NH_2 groups, apparently assume a planar disposition on the surface and in their presence the highest stationary potential $E = 1.02$–1.05 V is established on the charcoal. At a current of 0.25 mA g^{-1}, the shift of the electrochemical reduction potential of oxygen in the positive direction is more than 0.3 V.

A large group of relatively simple copper, cobalt, manganese, and iron complexes of *NN'*-disalicylidene-ethylenediamine, adsorbed on a pyrographite electrode, have been investigated. αα'-Bipyridyl and *o*-phenanthroline are known as ligands with a polyfunctional activity which can participate in the resonance transfer of electrons via systems of conjugated bonds. Furthermore, they are effective catalysts of the oxidation of various substrates by molecular oxygen in homogeneous systems.[128,129] Fig.9 illustrates the polarisation curves obtained at disc and ring electrodes for an approximately monolayer coverage of the disc electrode surface by the complex investigated. In the presence of cobalt complexes (curves *2*, *2'*, *3*, and *3'*) the half-wave potential shifts in the positive direction, but oxygen is reduced solely via the formation of hydrogen peroxide. When copper complexes are deposited (curves *4* and *4'*), the reaction proceeds both via the intermediate formation of hydrogen peroxide and with direct reduction to water, the ratio of the constants $K_1/K_2 = 0.23$ for $[Cu(5NO_2phen)]Cl_2$. The activity of the copper complexes depends on the degree of surface coverage by the latter and on the type of substituents. The activity is a maximum for a low coverage and falls when the coverage increases. This type of dependence can be explained if it is assumed, by analogy with homogeneous catalysis,[129] that the substrate (O_2) and the electrode surface are in the *cis*-conformation relative to the central ion of the adsorbed complex. The synchronous transfer of two electrons to the oxygen molecule is possible under these conditions. With increase of the degree of surface coverage, the possibility that such a conformation occurs diminishes, and the activity falls. Thus, in the case of phenanthroline complexes of copper, the role of the support (the carbon material) is manifested directly. The study of Vol'pin et al.[18] is the first in which it was possible to achieve the electrocatalysis of the oxygen reaction by organic copper complexes.

The tetrasulphonated phthalocyanine complexes of cobalt,[15,130] haemin and the chlorin e_6 complex of iron,[21] and the porphyrin complexes of iron and cobalt[131] exhibit a notable electrocatalytic activity in the cathodic reduction of oxygen.

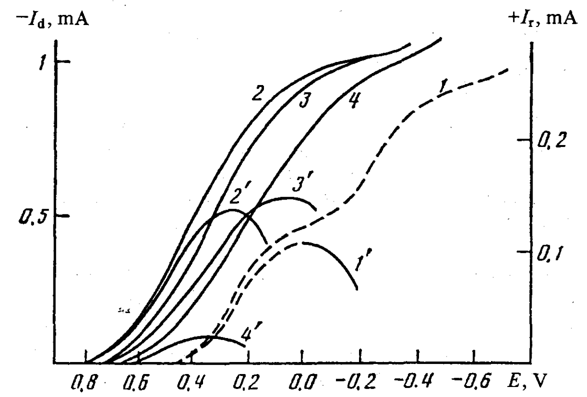


Figure 9. Polarisation curves for the electrochemical reduction of oxygen on a platinum disc electrode (curves *1*–*4*) and for the oxidation of hydrogen peroxide on a platinum ring electrode (curves *1'*–*4'*) in the absence (curve *1*) and presence of the complex adsorbed on the disc electrode:
2) cobalt–salen; *3*) cobalt–decamethyloctadehydrocorrin;
4) $[Cu(5NO_2phen)]Cl_2$.[18]

The mechanism of the reduction of oxygen by these substances differs little from that which obtains on carbon materials coated by a thick layer of the N_4-complexes.[130] The adsorbed phthalocyaninecobalt complex accelerates only the two-electron reaction and the phthalocyanineiron complex promotes the occurrence of the direct reduction to water.[130]

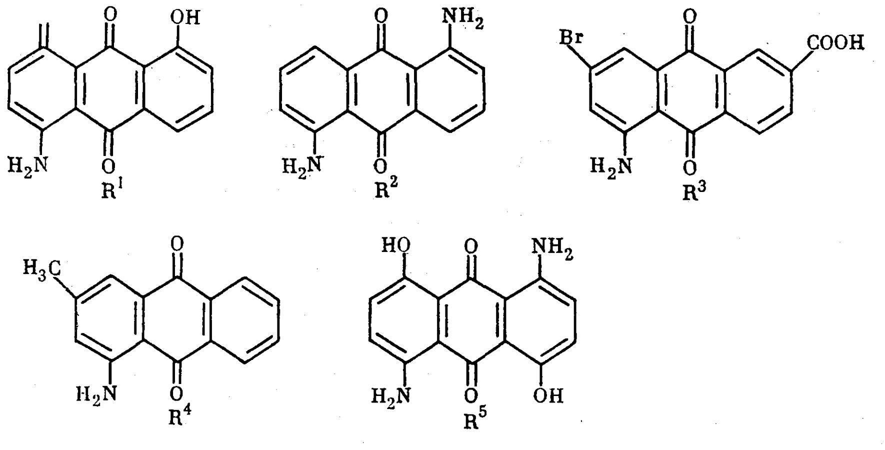


Figure 8. Different types of quinones used for the surface modification of carbon materials.[39]

In the region of high polarisation the slope of the $-\lg I-E$ plots is close to $2 \times 2.3\ RT/F$, which corresponds to slow addition of the first electron. For low polarisations, $\partial E/\partial \lg I$ ranges from $2.3\ RT/2F$ to $2.3\ RT/F$. According to the authors,[130,131] this is due to the approach to the O_2/HO_2^- equilibrium in alkaline electrolytes at low polarisations. According to Zagal et al.[130], such slow slopes can be accounted for also by the operation of different versions of the redox mechanism:

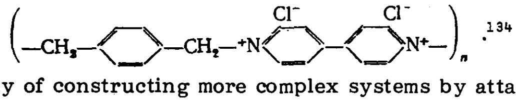
$$M^{III}OH + e \rightleftharpoons M^{II} + OH^- ,$$
$$M^{II} + O_2 \rightleftharpoons M^{III}{-}O_2^- ,$$
$$M^{III}{-}O_2^- + H_2O + e \rightarrow M^{III}{-}H_2O_2 + OH^- .$$

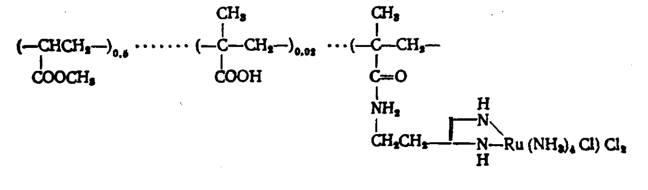
Unfortunately, lack of data for the surface coverage of the electrode by N_4-complexes hinders the quantitative comparison of the electrocatalytic properties of the complexes at a molecular level and the elucidation of the role of the carbon support.

Dinuclear complexes—covalently bound ("face to face") porphyrins—have been used recently[132] to modify the carbon surface. The activation of oxygen by these complexes can be represented schematically as follows:

$$LCo^{III}{-}Co^{III}L + 2e \rightarrow LCo^{II}{-}Co^{II}L ,$$
$$LCo^{II}{-}Co^{II}L + O_2 \rightarrow LCo^{II}{-}O{-}O{-}Co^{II}L ,$$
$$LCo^{II}{-}O{-}O{-}Co^{II}L + H^+ \rightarrow [LCo^{II}{-}OH{-}O{-}Co^{II}L]^+ ,$$
$$[LCo^{II}{-}OH{-}O{-}Co^{II}L]^+ + 2e + 3H^+ \rightarrow LCo^{III}{-}Co^{III}L + 2H_2O .$$

The 4-atom connecting chain between the ligands apparently corresponds to the optimum conditions for the coordination of the oxygen molecule between two cobalt atoms. When the monomer and the dinuclear cobalt dimer with the connecting fixed atom chain are adsorbed on pyrographite, the oxygen reduction reaction in an acid medium (0.5 M $HClO_4$ or $CF_3.COOH$) is accelerated compared with pure pyrographite, but proceeds via the intermediate formation of hydrogen peroxide. The quantity $\partial E/\partial \lg I \cong 2.3 \times 2RT/F$ agrees with the concept of the slow transition of the first electron.

The use in electrocatalysis of carbon electrodes modified by polymers constitutes an exceptionally promising trend. Polyfunctional electrocatalysts ensuring the simultaneous transfer of more than one electron in the slow stage, the optimum hydrophobic–hydrophilic environment in the active centres, and the reversibility of the protonation reaction can be created on their basis. However, despite the fact that an enormous number of studies on the electrochemical properties of polymer electrodes have been carried out, at the present time there have been only isolated studies devoted to electrocatalysis on such electrodes. The properties of polymeric acrylonitrile films on vitreous carbon and platinum have been investigated in the oxygen reaction.[133] Some acceleration of the electrochemical reduction of oxygen has been observed on the pyrographite electrode in the presence of a polymer coating made up of polyxylylviologen with a molecular weight of 11 000: .[134] The possibility of constructing more complex systems by attaching two active groups fulfilling different functions was reported in the same communication. The ruthenium(III) complex of the polymer is a highly active catalyst of the electrochemical reduction of hydrogen peroxide:



The complex is soluble in water but becomes insoluble at an electrolyte concentration in excess of 0.1 M. This makes it possible to obtain a stable polymer coating on the pyrographite surface. The complex $[Cu(o\text{-}phen)_2(ClO_4)_2]$, which is a highly effective catalyst of the two-electron reaction, is added to the immobilised polymer. Thus the simultaneous attachment to the pyrographite electrode of two active groups permits the creation of an electrocatalyst of the reduction of oxygen to water.

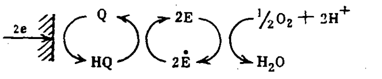
The PVP complex of copper shows a high catalytic activity in the cathodic reduction of oxygen.[43] However, its activity falls rapidly. Thus in the absence of current a potential of 1.15 V was recorded in the initial instance. The potential then shifts in the cathodic direction and is stabilised near 0.9 V. The stationary potential, established for charcoals modified by the complex, is higher than for pyrographite electrodes and reaches 1.2 V.

There is a correlation between the degree of saturation of the polymer by copper ions and the electrocatalytic activity, whose measure is the shift of the polarisation curve relative to the background curve. The extremum in the relation between the activity of the modified electrode and the pH (Fig.3, curve *1*) can be explained by taking into account data on the stability of the polymer complex. It has been shown[73,74] that copper mono- and di-pyridinate complexes are formed at pH 3–4 and are converted into the tetrapyridinate complexes at pH 5–6. One may therefore conclude that copper tetrapyridinate complexes exhibit catalytic activity. The pH dependence of the total amount of electricity corresponding to the redox transitions for the modified electrode (Fig.3, curve *2*) also passes through an extremum, which confirms the hypothesis that copper tetrapyridinate complexes are electrochemically active. The decrease of the amount of the active complex with alkaline pH can be explained by the decomposition of the catalytic complex with formation of copper hydroxide.

As the particle size of the highly disperse carbon materials increases, the catalytic activity of the complex also rises for low polarisations.[43] Having compared this result with data showing that the high-molecular-weight polymer (molecular weight 160000) is 2.5–4 times less active than the polymer having a lower molecular weight (50000), one may suppose that, depending on the ratio of the sizes of the polymer globule and the carrier particles, the character of the adsorption varies.[43] The difference between catalytic activities can be caused by the different macrokinetic characteristics of the highly disperse carbon catalysts and the polymers with different molecular weights deposited on them.

The most stable equilibrium oxygen potentials have been obtained using enzymes as modifying agents for the carbon surface.[2,22,23,27–29,135]

The mediator mechanism of the acceleration of the electrochemical reduction of oxygen, i.e.



has been achieved using a whole series of enzymes immobilised on carbon materials: peroxidase,[136] cytochrome c oxidase,[137] tyrosinase,[135] and laccase.[26]

In the case of the electron-transport protein cytochrome *c* [21] and also the enzymes tyrosinase [135] and laccase,[22,26] it has been possible to achieve a non-mediator mechanism of acceleration of this process in neutral solutions. The most reproducible data have been obtained with laccase. The adsorption of the enzyme on carbon black electrodes is almost irreversible. The parameters $\partial E/\partial pH$ and $\partial E/\partial \lg p_{O_2}$ for this electrode correspond to the coefficients of the Nernst equation for the O_2/H_2O pair. The small deviation from the theoretical equilibrium potential is apparently caused by the local increase of the pH in the layer of the adsorbed protein relative to the pH in the bulk of the solution.

The mechanism of the electrocatalytic reduction of molecular oxygen by immobilised laccase has been studied in detail.[97] The observed variation of the rate of reaction with the pH, the oxygen pressure (Fig.10), the concentration of laccase inhibitors (Fig.11), and temperature suggested the following mechanism of the activation of molecular oxygen in the electrode/laccase/oxygen system:

$$\begin{aligned}
&E + O_2 \rightarrow EO_2 && (\Delta E = 0.2 - 0.6\,V),\\
&EO_2 + e \rightleftharpoons EO_2^- ,\\
&EO_2^- + H^+ \rightarrow EO_2H && (\Delta E = 1.15 - 1.10\ V),\\
&EO_2H + 2e + H^+ \rightarrow EO^- + H_2O && (\Delta E = 1.20 - 1.15\ V),\\
&EO^- + e + H^+ \rightarrow EOH^-,\\
&EOH^- + H^+ \rightarrow E + H_2O\ .
\end{aligned}$$

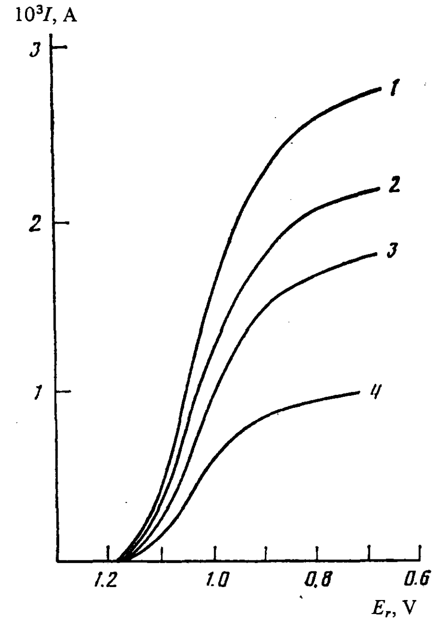


Figure 10. Polarisation curves for the electrochemical reduction of oxygen on an electrode with immobilised laccase at pH 4.5 and different oxygen partial pressures (atm): *1*) 1; *2*) 0.3; *3*) 0.25; *4*) 0.12.[97]

On the basis of the entire set of data, one may regard as entirely justified the claim that, in the region of low polarisations, the rate of electrochemical reduction of oxygen is limited by the rate of electron transfer stage, while in the region of the limiting current it is limited by the stage characteristic of enzyme catalysis. In the latter case, the dependences of the rate of the electrochemical reaction on the pH, the oxygen pressure, and the concentration of the inhibitors should be analogous to the experimentally observed dependences for the enzyme reaction[97] (Figs.10 and 11). In the region of low polarisations, the Tafel relation between the rate of reaction and the potential is observed, which shows that the electron transfer stage is slow.

The temperature variation is important for the elucidation of the mechanism of the cathodic reduction of oxygen on the enzyme electrode. In the first place, one should note that, over the entire potential range, the Arrhenius relation between the rate of reaction and temperature holds. The activation energy in the experimental potential range varies from 14.0 to 9.0 kJ mol^{-1} as the potential shifts in the cathodic direction (Fig.5).[97] Within the framework of the proposed mechanism of the electrocatalysis of the reduction of oxygen on the electrode with immobilised laccase, the rate-determining stage in the region of high polarisations is that characteristic of the enzyme reaction—this may be the binding (adsorption) of molecular oxygen to the active centre of laccase. The activation energy found in this range of potentials is virtually identical with the activation energy for the phenol oxidase reaction of the solubilised enzyme (10 kJ mol^{-1}). The activation energy for the solubilised enzyme was determined from the rate of oxidation of hydroquinone by atmospheric oxygen in the same temperature range as in the electrochemical reaction. Thus the conclusion that the slow stages in the enzyme reaction and in the biocatalytic reduction of oxygen are the same in the range of potentials more negative than 0.8 V has been confirmed.

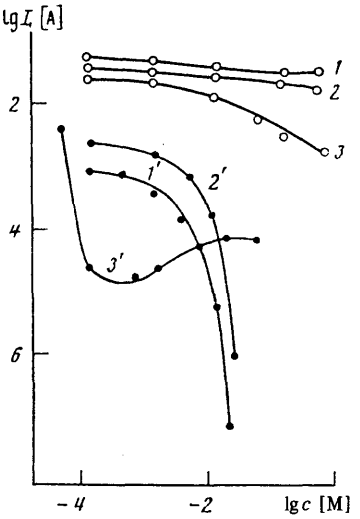


Figure 11. The influence of the concentration of inhibitors on the electrocatalytic activity of the electrode with immobilised laccase in the reduction of oxygen at pH 4.5; curves *1*–*3* were obtained for E = 0.8 V and curves *1'*–*3'* for E = 1.15 V in the presence of different ions: *1*) and *1'*) iodide; *2*) and *2'*) chloride; *3*) and *3'*) fluoride.[97]

In the region of low polarisations, the activation energy is likewise low. As shown above (Section IV), the rate-limiting stage is electron transfer from the active centre of the enzyme to the oxygen molecule.

Other examples of electrocatalysis on carbon electrodes modified by enzymes have also been described. In the presence of peroxidase adsorbed on pyrographite or carbon black,[23] a stationary potential ranging from 1.05 to 1.24 V is established in a hydrogen peroxide solution. Since the active centre of peroxidase (haemin) accelerates the reaction of H_2O_2 to an insignificant extent, peroxidase functions as the electrocatalyst, retaining its integrity and catalytic activity on immobilisation.

Comparison of data for the application of chemically modified carbon electrodes in electrocatalysis shows that the most important results have been achieved for enzyme electrodes. In the immediate future, one can probably expect the creation of active surface-modified electrodes on the basis of synthetic polymer systems. However, the lack of methods for the creation of such electrodes with an adequate chemical and electrochemical stability and activity in the anodic oxygen evolution reaction and other anodic reactions of electrochemical synthesis at high anodic potentials constitutes a serious gap. This problem is one of the most urgent in electrochemistry.

Analysis of the available data shows that the creation of electrodes on the basis of polymer systems closest to macromolecular biological systems is likely to be most useful.

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The Role of Peroxide Derivatives of the Elements in the Selective Catalytic Oxidation of Organic Substances

I.V.Spirina, V.P.Maslennikov, and Yu.A.Aleksandrov

Various mechanisms of the selective action of catalysts in the liquid-phase oxidation of organic substances are discussed. It is shown that the high selectivity of the autoxidation of organic substances catalysed by compounds of transition and non-transition elements is due to the interaction of the substrate being oxidised with the peroxide derivative of the element formed via the reaction between oxygen or the hydroperoxide product and the catalyst.
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I. INTRODUCTION

The oxidation of hydrocarbons and other organic substances by molecular oxygen is one of the principal ways of synthesising oxygen-containing chain compounds: aliphatic acids and alcohols, phenols, ketones, epoxides, etc. According to the ideas which have developed, this process is assigned to the class of degenerate-branched chain reactions; it leads to the formation of a large number of intermediates and final products.[1-3] The development of methods for the selective conversion of the petroleum raw material into oxygen-containing compounds under mild conditions is at present one of the most important tasks in chemical science.[4] As a rule, in order to increase the selectivity, the oxidation process is carried out in the presence of catalysts such as the salts of constant- and variable-valence elements, metal complexes, Lewis acids, etc. The study of the detailed mechanisms and kinetics of the above catalytic processes is therefore especially important for the solution of the problem of increasing selectivity.

The autoxidation of hydrocarbons in the presence of various catalysts has been the subject of numerous investigations and has been discussed in detail in a series of reviews and monographs.[2,3,5-11] Various mechanisms have been proposed in the literature for the action of catalysts in the liquid-phase oxidation of hydrocarbons. The increase of process selectivity in the presence of the catalyst is usually explained either by the milder reaction conditions, which is caused by the formation of a complex between oxygen or the hydroperoxide and the catalytic additive, and the subsequent decomposition of this complex with generation of free radicals, or by the appearance of new non-radical stages in the reaction of oxygen or the hydroperoxide activated in a complex with the catalyst.[5-11]

One of the mechanisms of the catalysis of oxidation reactions of organic compounds by derivatives of various elements, which ensures a high selectivity, involves the interaction of the substrate being oxidised with the peroxide derivative of the element formed via the reaction between oxygen or the hydroperoxide product and the catalyst.[12,13]

II. CATALYSIS OF FREE-RADICAL CHAIN OXIDATION REACTIONS OF HYDROCARBONS

The catalytic action of variable-valence metal compounds in chain oxidation reactions of hydrocarbons has been investigated in detail and is widely used.[2,3,5-10] The most important details of the mechanism of these reactions have been reliably demonstrated. Thus it is generally recognised that metal compounds can participate in any stage of a degenerate-branched chain oxidation reaction of a hydrocarbon: initiation, chain propagation, or chain branching.[2,3,6,7,11]

The principal radical formation reaction in the oxidation chain initiation stage in the presence of a catalyst is the activation of oxygen and the interaction of the resulting oxygen-containing metal (M) complex with the hydrocarbon:[3,6,7,11]

$$M^{n+} + O_2 \rightleftharpoons M^{(n+1)+}O_2^{\dot{-}} \; ;$$
$$M^{(n+1)+}O_2^{\dot{-}} + RH \rightarrow M^{n+} + HO_2^{\cdot} + R^{\cdot} \; .$$

The free-radical chain oxidation of hydrocarbons is catalysed via this mechanism by low-valence complexes of iridium, rhodium, ruthenium, osmium, platinum, etc.[14-16]. The occurrence of this type of initiation has been demonstrated using inhibitors in relation to the oxidation of ethylbenzene in the presence of nickel bis(acetylacetonate)[17] and has been confirmed in a study of the oxidation of cumene catalysed by *o*-phenanthroline complexes of copper.[18]

The commonest method for chain branching in oxidation by compounds of various elements presupposes catalysis of the homolytic decomposition of the primary hydrocarbon oxidation products, namely hydroperoxides.[2]

The catalysis by variable-valence metals is based on one-electron oxidation-reduction reactions between metals ions and the hydroperoxide:[2,3,6,11]

$$ROOH + M^{n+} \rightarrow RO^{\cdot} + M^{(n+1)+} + HO^{-} \; ;$$
$$ROOH + M^{(n+1)+} \rightarrow RO_2^{\cdot} + M^{n+} + H^{+} \; .$$

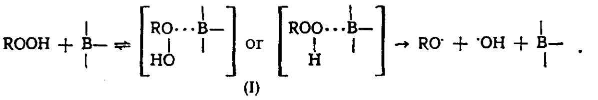
It has been shown[10, 19-22] that Lewis acids and compounds of alkali and alkaline earth metals can also induce the radical decomposition of hydroperoxides. The mechanism of the catalytic action of Lewis acids and constant-valence metal salts in the autoxidation reactions of hydrocarbons has been inadequately investigated. The existence of two alternative pathways has been postulated: the homolysis of the hydroperoxide bound in a complex with the catalyst and the bimolecular interaction of this adduct with a second hydroperoxide molecule:[10,19-22]

$$ROOH \cdot Ct \rightarrow RO^{\cdot} + HOCt;$$
$$ROOH \cdot Ct + ROOH \rightarrow RO^{\cdot} + H_2O \cdot Ct + RO_2^{\cdot} \; .$$

where Ct is a Lewis acid or a constant valence metal ion. Furthermore, radicals may be generated in the interaction of the complex with the substitute being oxidised, for example styrene:[19]

$$ROOH \cdot Ct + H_2C{=}CHC_6H_5 \rightarrow ROCH_2\dot{C}HC_6H_5 + HOCt^{\cdot} \; .$$

The ability of boron compounds to increase the yield of secondary alcohols in the liquid-phase autoxidation of paraffins has been known for a long time.[23] However, the mechanism of this process has not been treated unambiguously. According to some investigators,[24–26], the complex formation reaction between the catalyst and the hydroperoxide accelerates the reaction of ROOH with formation of free radicals initiating new chains:

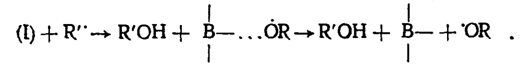


$$\mathrm{ROOH} + \underset{|}{\overset{|}{\mathrm{B}}}{-} \rightleftharpoons \left[\begin{array}{c}\mathrm{RO}\cdots\underset{|}{\overset{|}{\mathrm{B}}}{-}\\ |\\ \mathrm{HO}\end{array}\right] \text{ or } \left[\begin{array}{c}\mathrm{ROO}\cdots\underset{|}{\overset{|}{\mathrm{B}}}{-}\\ |\\ \mathrm{H}\end{array}\right] \rightarrow \mathrm{RO}^{\cdot} + {}^{\cdot}\mathrm{OH} + \underset{|}{\overset{|}{\mathrm{B}}}{-}\ .$$

(I)

The preferential formation of alcohols in the oxidation of alkanes catalysed by boron compounds takes place, according to Wolf et al.,[27] as a result of the decomposition of the hydroperoxide coordinated to the catalyst induced by solvent radicals:

$$\mathrm{RO^{\cdot}(HO^{\cdot}) + R'H \rightarrow ROH(H_2O) + R'^{\cdot}}\ ;$$



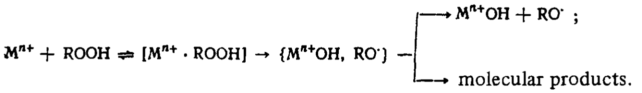
$$(\mathrm{I}) + \mathrm{R'^{\cdot}} \rightarrow \mathrm{R'OH} + \underset{|}{\overset{|}{\mathrm{B}}}{-}\ldots\dot{\mathrm{O}}\mathrm{R} \rightarrow \mathrm{R'OH} + \underset{|}{\overset{|}{\mathrm{B}}}{-} + {}^{\cdot}\mathrm{OR}\ .$$

Thus the primary step in the catalytic initiation and branching of oxidation chains is complex formation between the catalyst and oxygen or the hydroperoxide product, which leads to the activation of the oxidant. The catalyst makes it possible to carry out the oxidation at high rates under milder conditions. However, there is no significant increase in the selectivity of the process as a result of its being achieved via a free-radical mechanism.[3] The mixture of oxidised products contains in this case various oxygen-containing substances.

III. MOLECULAR SELECTIVE CATALYTIC OXIDATION REACTIONS OF HYDROCARBONS

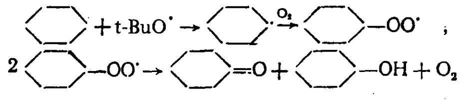
1. The Mechanisms of the Selective Catalytic Oxidation of Hydrocarbons with Participation of the Catalyst–Hydroperoxide Complex

In the autoxidation reactions of hydrocarbons, catalysts not only influence the rate of oxidation but also change the ratios of the products formed in the reaction, increasing the process selectivity. Thus the catalytic acceleration of the decomposition of organic hydroperoxides by copper, cobalt, nickel, chromium, molybdenum, and vanadium compounds increases the content of ketones in the reaction mixture.[28–34] In this case the radical decomposition is accompanied also by the molecular decomposition of the hydroperoxides, whose contribution can reach 90%. Both pathways in the catalytic decomposition of hydroperoxides involve the formation of the same catalyst–hydroperoxide complex.[29,32–34] The molecular decomposition is an example of the manifestation of the "cage effect": some of the radicals formed in the solvent cage interact with the metal ions affording molecular products, while others are released into the surrounding space:[3,11,34]



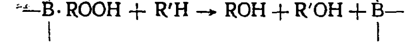
$$\mathrm{M^{n+} + ROOH \rightleftharpoons [M^{n+}\cdot ROOH] \rightarrow \{M^{n+}OH,\ RO^{\cdot}\}} \rightarrow \begin{cases}\mathrm{M^{n+}OH + RO^{\cdot}}\ ;\\ \text{molecular products.}\end{cases}$$

In the study of the decomposition of organic hydroperoxides catalysed by cobalt, chromium, vanadium, boron, molybdenum, titanium, etc. compounds the oxidation of the hydrocarbon used as the solvent has been observed, which leads to an increased content of alcohols or ketones in the reaction mixture.[35–41] According to Sheldon and Van Doorn,[35] up to 50% of cyclohexanol and cyclohexanone in the products of the decomposition of t-butyl hydroperoxide in cyclohexane in the presence of variable valence metal stearates and acetylacetonates is formed as a result of radical processes:



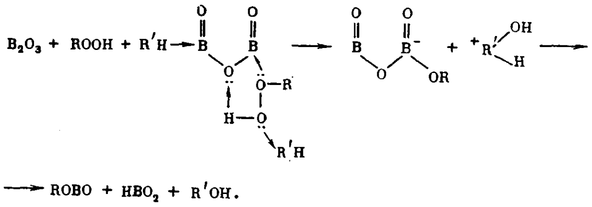
However, it has been shown[36] that the oxidation of nonane and cyclohexane by t-butyl hydroperoxide, catalysed by transition metal compounds and involving the formation of ketones and cyclohexanol, proceeds without the participation of free t-butoxy-radicals.

According to Pek Lak Von et al.,[39] only a small proportion of the radicals (10–15%) formed in the decomposition of the hydroperoxide bound in a complex with borate are released into the surrounding space and ensure the initiation of the oxidation process. The preferential accumulation of alcohols in this instance takes place as a result of the non-radical decomposition of the complex of the hydroperoxide with the catalyst in its bimolecular interaction with the paraffin:



$$-\underset{|}{\overset{|}{\mathrm{B}}}\cdot\mathrm{ROOH} + \mathrm{R'H} \rightarrow \mathrm{ROH} + \mathrm{R'OH} + \underset{|}{\overset{|}{\mathrm{B}}}{-}\ . \qquad (1)$$

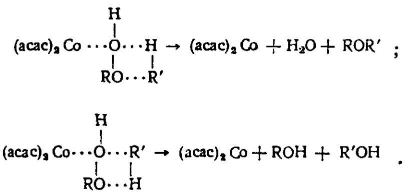
It has been suggested[40] that the catalysis of the oxidation of hydrocarbons by boron trioxide proceeds via an electrophilic substitution mechanism:



(2)

According to Eqns.(1) and (2), the increased yield of alcohols is caused by the formation of two alkanol molecules—one from the hydroperoxide and the other directly from the paraffin.

The participation of hydrocarbons with a labile C–H bond in the decomposition of cumenyl hydroperoxide catalysed by cobalt acetylacetonate has been described.[41] A mechanism has been proposed according to which the hydroperoxide forms a coordinate bond with the catalyst and there is simultaneous activation of the hydrocarbon forming part of the composition of the solvate shell of the adduct. The ternary complexes formed decompose via a non-radical mechanism:



$$\mathrm{(acac)_2Co\cdots\underset{\displaystyle\underset{|}{RO}}{\overset{\displaystyle\overset{H}{|}}{O}}\cdots\underset{\displaystyle\underset{|}{\cdots R'}}{H}} \rightarrow \mathrm{(acac)_2Co + H_2O + ROR'}\ ;$$

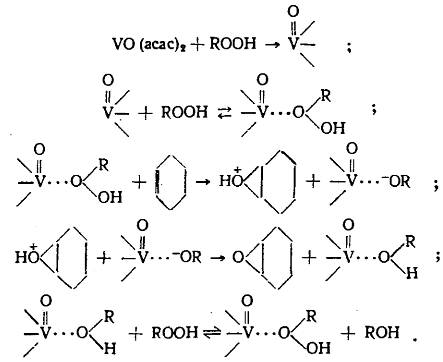
$$\mathrm{(acac)_2Co\cdots\underset{\displaystyle\underset{|}{RO}}{\overset{\displaystyle\overset{H}{|}}{O}}\cdots\underset{\displaystyle\underset{|}{\cdots H}}{R'}} \rightarrow \mathrm{(acac)_2Co + ROH + R'OH}\ . \qquad (3)$$

The contribution of molecular decomposition to the overall reaction of the hydroperoxide depends on the nature of the solvent and increases with decrease of the strength of the C–H bonds in the hydrocarbon. Thus cumenyl hydroperoxide reacts to the extent of 40% via the molecular pathway in ethylbenzene.[41] Since methylphenylmethanol was not detected among the reaction products, the authors[41] believe that the process proceeds via the mechanism (3).

Thus the significant increase of the selectivity of the autoxidation of hydrocarbons occurs when, together with the homolytic decomposition of the hydroperoxide bound in a complex with the catalyst, there is a possibility of its reaction via the molecular mechanism. The molecular pathway in many instances is an example of the "cage effect". Certain catalysts are capable of involving the hydroperoxide in an oxidation reaction via the C–H bonds of the hydrocarbon, which leads to an increased yield of oxygen-containing products. It has been suggested[41] that this process represents molecular interaction of the catalyst–hydroperoxide complex with the solvent.

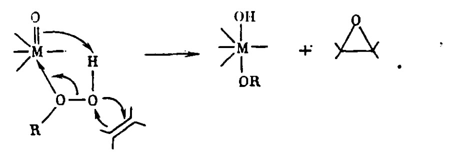
The high selectivity of the catalytic epoxidation of olefins by hydroperoxides is also caused by the molecular character of the process. This is indicated by the lack of influence by oxygen on the rate of epoxidation, the passivity in this reaction of catalysts reacting with hydroperoxides to form free radicals, and the stereospecificity of the catalytic epoxidation. The absence of a single point of view on the mechanism of this process is noteworthy; only the involvement in it of the metal in the highest oxidation state is not open to doubt.[9,42,43,46]

According to some investigators,[9,35,42–48] the catalytically active species in these processes is the complex of the catalyst with a hydroperoxide molecule, with the aid of which oxygen is transferred to the olefin. Thus a mechanism has been proposed for the epoxidation of cyclohexene by t-butyl hydroperoxide in the presence of vanadyl acetylacetonate,[44] according to which the first stage involves the rapid activation of the metal by the hydroperoxide, i.e. the transition of the metal to the highest valence state. This is then followed by the rapid and reversible formation of an active complex of the catalyst with a hydroperoxide molecule. The complex formation reaction induces the heterolysis of the O–O bond with transfer of the hydronium cation to the substrate. The elimination of a proton and its transfer to the alkoxide anion, bound to the complex, lead to the formation of the olefin oxide and the catalyst–alcohol complex. The interaction of this complex with the hydroperoxide entails ligand exchange and the regeneration of the active species:[44]

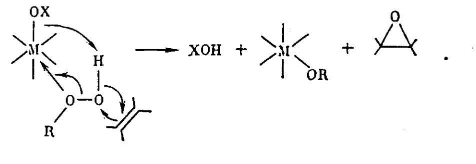


An analogous mechanism has been proposed[35] for the epoxidation of cyclohexene by t-butyl hydroperoxide catalysed by $Mo(CO)_6$. According to Sheldon,[43] catalysts based on tungsten(VI), vanadium(V), and titanium(IV), act in the same way.

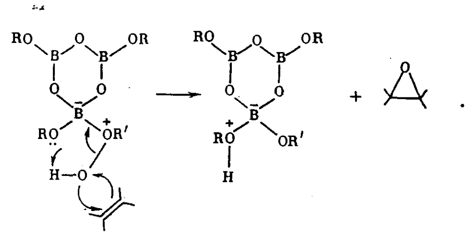
From the parallel variation of the electron-accepting properties of the catalytic additive and the rate constants for the epoxidation reaction, it has been suggested[27,35,47,48] that the function of the catalyst is to withdraw electron density from the oxygen atoms of the peroxide bridge, i.e. the catalyst acts in this instance as a Lewis acid. Two probable mechanisms have been proposed for the reaction of the catalyst–hydroperoxide complex with the olefin.[35] For compounds containing the M=O fragment, the process proceeds via a cyclic transition state:



The second mechanism has been proposed for compounds containing the M–OX (X = H, R) group, which acts as a proton acceptor:[35]



The epoxidation of olefins by alkyl hydroperoxides in the presence of metaborates has been explained analogously:[27,47–49]



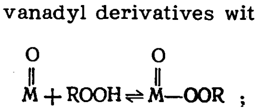
Consequently the molecular conversion of the hydroperoxide coordinated to the catalyst in the reaction with the saturated or unsaturated compound to form oxygen-containing products can be the cause of the high selectivity of the catalytic autoxidation of hydrocarbons and the epoxidation of olefins. The formation of complexes of the hydroperoxide with the compounds of transition and non-transition elements used as catalytic additives has been demonstrated by kinetic and physicochemical methods.[3,11,22,26,32] However, the numerous experimental data obtained do not conflict with the hypothesis that peroxide derivatives of the elements participate in selective catalytic processes.

2. The Involvement of Peroxide Derivatives of the Elements in Selective Catalytic Processes

(a) *The formation of intermediate alkyl peroxide derivatives of the elements in the liquid-phase catalytic oxidation of hydrocarbons.*

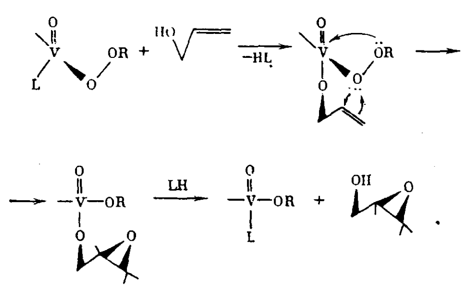
According to Mimoun[12] and Spirina et al.,[13] organoelemental peroxides play an active role in the hydroperoxide epoxidation of olefins and their conversion into ketones, catalysed by added compounds of non-transition and transition elements.

Thus in the middle 1970s, it was suggested[50,51] that, in the epoxidation of olefins in the presence of molybdenum and vanadium compounds, the accumulation of the peroxides of these elements may be a result of the reactions of the corresponding molybdenyl and vanadyl derivatives with the alkyl hydroperoxide:



$$\overset{O}{\overset{\|}{M}} + ROOH \rightleftharpoons \overset{O}{\overset{\|}{M}}{-}OOR\ ;\quad M{=}Mo,\ V\ .$$

The higher reactivity of allyl alcohols compared with olefins and their high *syn*-selectivity indicate the participation of the peroxides of transition elements in the catalytic epoxidation of unsaturated compounds.[42,52–55] In this case one of the ligands in the organo-metallic peroxides is substituted by the allyloxy-fragment and the epoxidation takes place intramolecularly, the disposition of the reacting fragments favouring the formation of the *syn*-epoxyalcohol:



(4)

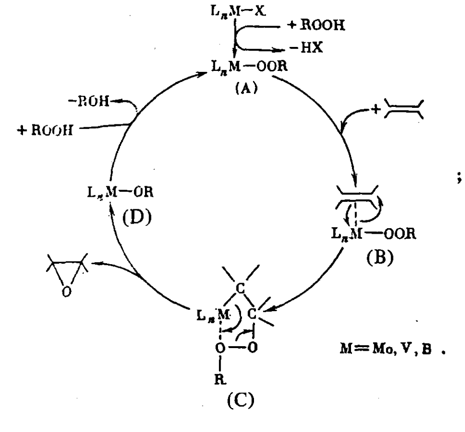
The high stereoselectivity of the epoxidation of aryl-alcohols by t-butyl hydroperoxide in the presence of tri(t-butoxy)aluminium is caused also by the participation of organo-elemental peroxides in this process, whose mechanism is assumed to be analogous to Scheme (4).[56]

From the results obtained in a number of studies,[57–60] the catalytic cycle illustrated in Scheme I has been proposed to explain the epoxidation of olefins and allyl alcohols by hydroperoxides, catalysed by molybdenum, vanadium, and boron compounds.[12] It is suggested that the active species in the reaction are the organometallic peroxides (A). The process involves the formation of a complex of the unsaturated compound with the peroxide of the given element (B), which is accompanied by the peroxymetallation of the substrate. This reaction proceeds via the formation of a five-membered peroxometallocyclic intermediate (C), which decomposes to the epoxy-compound and the alkoxy-derivative of the metal (D). The interaction of the alkyl hydroperoxide with compound (D) leads to the regeneration of the initial organoelemental peroxide (A).

However, the occurrence of the stage involving the formation of compound (B) in catalysis by boron compounds is in our view extremely unlikely, since, according to Nesmeyanov and Sokolik,[61] the addition of an alkene to an organoboron compound is possible only at the boron–carbon bond at temperatures in excess of 100 °C. The olefin is not inserted in the boron–oxygen bond.

The possibility of the formation of intermediate peroxide derivatives of vanadium and cobalt in catalytic liquid-phase oxidation reactions of hydrocarbons has been postulated[62,63] from kinetic data obtained in the study of the reactions of t-butyl and cumenyl hydroperoxides in the presence of cobalt and vanadium acetylacetonates.

Scheme I



According to Makin et al.,[64] the interaction of borates with hydroperoxides leads to the establishment of the equilibrium

$$\mathrm{ROOH+B(OR')_3 \rightleftharpoons B(OOR)(OR')_2+R'OH} \qquad (5)$$

Direct proof of the formation of alkyl peroxide derivatives of boron, vanadium, molybdenum, and tungsten in the reactions of alkyl peroxides with the derivatives of these elements and their participation in selective oxidation reactions has been obtained.[65–72]

The study of the interaction of a mixture of t-butyl hydroperoxide with the organoborane $R_mB(OR')_{3-m}$, where $m = 0 - 2$, $R = C_3H_7$, C_5H_{11}, or C_6H_5, and $R' = C_4H_9$ [65–88] or with derivatives of quadrivalent or quinquevalent vanadium [$V(OC_4H_9)_4$ and $VO(OC_4H_9\text{-t})_3$][69,70] by IR and ^{1}H NMR spectroscopy demonstrated that the alkoxy-group is exchanged for the alkylperoxy-fragment in the system. It is preceded by complex formation between the reactants. Depending on the nature of the organo-elemental compound, the process takes place during a fraction of a second or over a period of several minutes. The yield of the alkyl peroxide derivative of the element for the equimolar reactant ratio at 20 °C is between 10 and 90%.[65–70] Organoelemental peroxide derivatives of boron, aluminium, silicon, vanadium(V), and cobalt(III) have been obtained by a reaction analogous to reaction (5).[13,69,73–75]

The study of the oxidation of alkanes by t-butyl hydroperoxide catalysed by boron, aluminium, silicon, titanium, vanadium, and palladium compounds[13,69,76–80] demonstrated that at 50–160 °C paraffins are converted into oxygen-containing products—aliphatic alcohols and ketones, in nearly quantitative yields (Table 1).

Table 1. The yields of the products of the oxidation of paraffins by the system t-butyl hydroperoxide—derivative of the element (in moles per mole of the peroxide which has reacted).

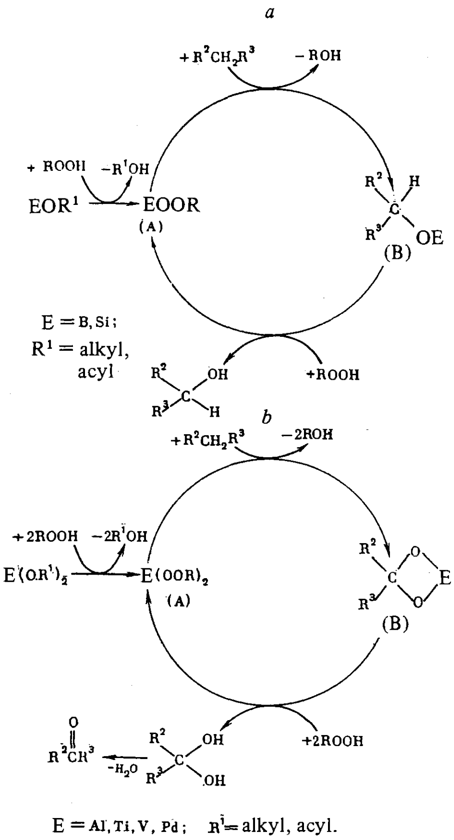
Paraffin	c_{hp}, M	Element-containing additive	c_a, M	t, °C	Yield: alkanols	Yield: alkanones	Refs.
Dodecane	0.10	$(C_4H_9O)_3B$	0.10	150	0.48	—	[76]
Octane	0.10	$(C_3H_3F_4O)_3B$	0.10	130	0.98	—	[80]
Pentane	0.10	$(t\text{-}C_4H_9O)_3Al$	0.01	50	—	0.49	[77]
Nonane	0.10	$(C_4H_9O)_4Si$	0.10	160	0.84	—	[80]
Nonane	0.10	$(C_4H_9O)_4Si$	0.05	140	0.42	0.11	[80]
Octane	0.10	$(C_4H_9O)_4Ti$	0.005	60	0.02	0.29	[79]
Octane	0.12	$(t\text{-}C_4H_9O)_3VO$	0.02	50	—	0.30	[69, 78]
Octane	0.10	$(CF_3COO)_2Pd$	0.01	60	—	0.40	[79]

Notation: c_{hp} is the concentration of t-butyl hydroperoxide and c_a the concentration of the additive.

The oxidation of hydrocarbons by alkyl hydroperoxides in the presence of catalysts—alkoxy— or acyloxy-derivatives of the elements—can be achieved in the catalytic cycles illustrated in Scheme II. The boron and silicon compounds in cycle *a* catalyse mainly the conversion of paraffins into secondary alcohols. Cycle *b* operates in the catalysis of the oxidation of hydrocarbons by derivatives of aluminium, titanium, vanadium, and palladium, which leads to aliphatic ketones. The oxidising agents in this process are the organoelemental peroxide (A), which interacts with the C–H bonds of the substrate to form organoelemental compounds containing a fragment of the hydrocarbon oxidised (B), and the alcohol corresponding to the hydroperoxide. The element-containing derivative (B) gives rise to the oxidation product (the alcohol or ketone) under the influence of the excess hydroperoxide and the initial organoelemental peroxide is regenerated. The operation of Scheme II has been confirmed also by the fact that the products of the oxidation of paraffins by the alkyl hydroperoxides–organoelemental compound system (with the equimolar reactant ratio) contain no free alcohols or ketones, with the hydrocarbon skeleton corresponding to the initial alkane.[79,80]

These compounds are formed either when an excess of the hydroperoxide is used or as a result of the hydrolysis of the reaction mixture.

Scheme II



In order to confirm the participation of organoelemental peroxides in catalytic oxidation processes, a detailed study has been made[13,69,76–80] of one of the stages in the catalytic autoxidation of hydrocarbons—the thermal decomposition of a series of alkyl peroxide derivatives of boron, aluminium, silicon, vanadium, and palladium in solutions in paraffin. It was found that the peroxides of these elements interact with hydrocarbons to produce in the hydrolysed reaction mixture high yields of the oxidation products identical with the oxygen-containing compounds obtained in the hydroperoxide oxidation of alkanes catalysed by non-peroxide derivatives of the elements (Tables 1 and 2).

The character and structure of the peroxide derivative and also its state in solution determine the composition of the hydrocarbon reaction products. Thus boron and silicon monoperoxides oxidise paraffins with a high selectivity to organoelemental compounds, which affords secondary aliphatic alcohols after hydrolysis.[80,81] The introduction into the molecule of the peroxide of the given element of one or two additional alkylperoxy-groups leads to the accumulation of aliphatic ketones together with alcohols in the hydrolysed reaction mixture.[76,79–81] The oxidation of alkanes by aluminium, vanadium, or palladium peroxide leads to the preferential formation, under mild conditions, of element-oxyderivatives, which hydrolyse to the isomeric ketone.[77–80]

Table 2. The yields of the products of the oxidation of paraffins by element peroxides (in moles per mole of the peroxide which has reacted, after the hydrolysis of the reaction mass).

Paraffin	Peroxide*	c_0 **	t, °C	Yield: s-alkyl-alcohols	Yield: alkanones	Refs.
Dodecane	$(C_4H_9O)_2BOOR$	0.10	150	0.48	—	[79]
Octane	$(C_3H_3F_4O)_2BOOR$	0.10	130	0.98	—	[80]
Nonane	$C_4H_9B(OOR)_2$	0.05	140	1.66	0.15	[81]
Octane	$(C_2H_5O)_2AlOOR$	0.02	70	—	0.01	[77]
Octane	$(t\text{-}C_4H_9O)_2AlOOR$	0.04	70	—	0.15	[77]
Nonane	$(C_4H_9O)_3SiOOR$	0.08	160	0.84	—	[80]
Nonane	$(C_4H_9O)_2Si(OOR)_2$	0.05	140	0.83	0.22	[80]
Octane	$(t\text{-}C_4H_9O)_2V(O)OOR$	0.03	20	—	0.42	[69]
Octane	$CF_3C(O)OPdOOR$	0.002	80	—	0.50	[79]

*R = t-C_4H_9.
**Initial peroxide concentration.

The peroxides of elements are capable of more than the oxidation of saturated hydrocarbons at the C–H bond. They interact with alkenes to form olefin oxides and methyl ketones,[12,71,72,82–87] they oxidise ethers to acetals[88] and alcohols to aldehydes and ketones;[56,75] they hydroxylate aromatic and unsaturated compounds[80,89,90] and they lead to the ring expansion in cyclic acetals, converting them into diol monoethers[91] (Table 3).

Table 3. The yields of the products of the oxidation of organic substances by element peroxides (in moles per mole of the peroxide which has reacted, after the hydrolysis of the reaction mass).

Peroxide*	Substrate oxidised	t, °C	Product	Yield	Refs.
$(C_4H_9O)_2BOOR$	Dibutyl ether	90	Acetals of butyraldehyde	0.56	[88]
$(C_4H_9O)_2BOOR$	Anisole	90	*o*- and *p*-methoxyphenols	0.99	[90]
$(C_4H_9O)_2BOOR$	Butyl phenyl ether	90	*o*- and *p*-butoxyphenols	0.97	[88[
$(C_4H_9O)_2BOOR$	Toluene	90	*o*- and *p*-cresols	0.80	[90]
$(C_4H_9O)_2BOOR$	Mesitylene	90	Mesitol	0.85	[90]
$(C_4H_9O)_2BOOR$	Oct-1-ene	120	1,2-Epoxyoctane	0.97	[82]
$(C_3H_3F_4O)_2BOOR$	Mesitylene	80	Mesitol	0.99	[90]
$(C_4H_9O)_3SiOOR$	Mesitylene	150	Mesitol	0.06	[80[
$(C_4H_9O)_3SiOOR$	Oct-1-ene	150	1,2-Epoxyoctane and s-octenyl alcohols	0.08 0.46	[80]
$CF_3C(O)OPdOOR$	Oct-1-ene	20	Hexyl methyl ketone	0.90	[84—86]
$(PPh_3)_2Pt(CH_3)OOR$	Oct-1-ene	80	Hexyl methyl ketone	0.80	[87]
$(CH_3)_2GaOOR$	Hex-1-ene	120	1,2-Epoxyhexane	0.80	[83]

*R = t-C_4H_9.

The data described above make it possible to explain fairly reliably the decrease of the rate of reaction observed in the autoxidation of alkanes in the presence of boron-containing additives, with simultaneous increase of the yield of secondary alcohols.[23] The alkyl hydroperoxide accumulated in the autoxidation of the paraffin reacts with the catalyst to form an organoboron peroxide. The probability of chain branching in the oxidation process then diminishes, because the homolytic decomposition of the boron peroxide proceeds at higher temperatures than the decomposition of the corresponding alkyl hydroperoxide. The molecular reaction of the organoboron peroxide with the initial alkane is accompanied by the formation of secondary alcohols, which increases the selectivity of the oxidation reaction.

(b) *The mechanisms of the oxidation of organic compounds at the C–H bond by alkyl peroxides and peroxo-complexes of the elements.*

In the study of the interaction of organoelemental peroxides (Table 2) with organic compounds it has been observed that the oxidation of the substrate is accompanied by the disappearance of peroxide oxygen.[13,69,76–81] Analysis of the composition of the products of the decomposition of the element peroxides in various organic solvents and also the character of their accumulation show that the element peroxides react via two parallel pathways in solutions in organic compounds:

1) via the oxidation of the solvent:

$$EOOR + HR' \rightarrow EOR' + ROH;$$

2) homolytically with dissociation of the peroxide bond:

$$EOOR \rightarrow EO^{\bullet} + \dot{O}R.$$

The interaction of an organoelemental peroxide with the hydrocarbon used as the solvent was observed for the first time in the thermal decomposition of t-butylperoxytriethylstannane in n-dodecane.[92]

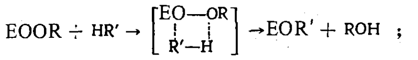
The kinetic parameters of the oxidation of organic substances by organoelemental peroxides and of the homolytic decomposition of peroxide compounds have been determined.[80–82,88,90] The activation energy for the homolytic cleavage of the peroxide bond is significantly higher (by 10 to 20 kcal mol^{-1}) than the activation energy for the interaction of element-containing peroxides with organic compounds. The decrease of the yield of the oxidation products with increase of the process temperature is consistent with this finding.[13]

It has been demonstrated by a thermochemical method that the reaction of organoelemental peroxides in solutions in ethers and in unsaturated and aromatic compounds proceeds via the preliminary formation of a complex of the peroxide with a solvent molecule. The constants for the complex formation reactions of t-butylperoxydi(butoxy)borane with organic substances, calculated by the method of Becker et al.,[93] range from 0.16 to 0.35 litre mol^{-1} (at 20 °C).[80,94] The 1 : 1 complex formed then decomposes as a result of the oxidation of the organic substrate or homolytically, generating two hydroxy-radicals.[13,80,88,90]

As stated above, organoelemental peroxides interact with the organic substances being oxidised to form element alkoxide derivatives of the substrate. When the reactions proceed via a free-radical mechanism, these compounds can accumulate only on decomposition of the organoelemental peroxide compound induced by solvent radicals R'$^{\bullet}$:

$$EOOR + R'^{\bullet} \rightarrow EOR' + RO^{\bullet}.$$

However, the reaction rate constant is independent of the initial peroxide concentration and remains unchanged when inhibitors of free-radical reactions (galvinoxyl, ionol) are introduced into the system.[80,82,88,90] Furthermore, as the process temperature is reduced, the yield of oxidation products increases. Consequently, hydroxy-derivatives of the elements, containing the substrate radical, appear in reactions involving the oxidation of organic compounds by organoelemental peroxides in the absence of the induced decomposition of alkyl peroxide derivatives of the elements. They are formed via the molecular mechanism (6) or the cryptoradical mechanism (7):



$$EOOR + HR' \rightarrow \left[\begin{array}{c} EO—OR \\ \vdots \qquad \vdots \\ R'—H \end{array}\right] \rightarrow EOR' + ROH \quad ; \qquad (6)$$

$$EOOR + HR' \rightarrow \{EO^{\bullet} + R'^{\bullet} + ROH\} \begin{cases} \rightarrow EOR' + ROH \; ; \\ \rightarrow EO^{\bullet} + R'^{\bullet} + ROH \; . \end{cases} \qquad (7)$$

The rate of release of radicals from the solvent cage is then correlated with the variation of the viscosity of the medium.[10] The study of the influence of the viscosity of the medium on the interaction of t-butylperoxydi(butoxy)borane with a series of hydrocarbons ranging from hexane to hexadecane at 150 °C[80] revealed that a change in solvent viscosity from 0.168 to 0.532 cP does not affect the kinetic parameters and the yield of the products of this reaction (Table 4). The data in Table 4 support the molecular mechanism, but they can also arise from a cryptoradical process when the cage effect is manifested in this reaction to an inadequate extent.

Table 4. The influence of the viscosity of the medium η on the oxidation of alkanes by t-butylperoxydi(butoxy)borane at 150 °C and an initial peroxide concentration of 0.10 M.[80]

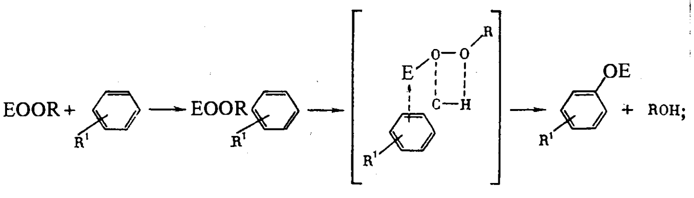
Hydrocarbon	η_{150}, cP	$10^5 k_{\mathrm{eff}}$, s^{-1}	W, mol mol^{-1}	$10^7 k_{\mathrm{ox}}$, litre mol^{-1}s^{-1}
Octane	1.168	3.0	0.48	3.0
Decane	0.249	3.1	0.46	3.3
Dodecane	0.339	3.2	0.48	3.1
Tridecane	0.380	3.1	0.45	3.3
Hexadecane	0.532	3.3	0.47	3.2

Notation: W is the yield of s-alkyl alcohols, k_{eff} the effective rate constant for the disappearance of the peroxide oxygen, and k_{ox} the rate constant for the oxidation of alkanes.

In the study of the oxidation of mesitylene by t-butylperoxydi-(1,1,3-trihydrotetrafluoropropoxy)borane in magnetic fields with an induction of 0.05–0.4 T, it was observed that the yield of mesitol diminishes by 5–15% compared with the yield in the Earth's magnetic field.[95] This effect can be explained as follows. The peroxide investigated reacts via two parallel pathways in solutions in organic substances: via the oxidation of the substrate and homolytically with formation of two hydroxy-radicals. The magnetic field acts on the liquid-phase radical reactions at the stage involving the recombination of two radicals in the cage. The rate of transition of the radical pairs from the singlet to the triplet state and the fraction of these states and ultimately also the yield of the product of the recombination within the cage depend on the induction of the magnetic field. In the oxidation of mesitylene by an organoboron peroxide, which proceeds via a cryptoradical or molecular mechanism, the yield of mesitol is independent of the induction of the magnetic field. On the other hand, the rate of the parallel process in which radicals are released from the cage (via the triplet state) varies with the induction, which leads to the observed magnetic effect.

Thus the results obtained in the study of the influence of the viscosity of the medium and of the magnetic field on the oxidation of organic substances by element peroxides indicate the molecular character of the interaction of organoelemental peroxides with organic substrates.

The molecular mechanism of this process has also been confirmed by data for the oxidation of aromatic compounds by element peroxides. In the study of the hydroxylation of toluene and mesitylene by organoelemental peroxides at 90 °C [80,90,95] no products of the interaction of the radicals $EO^{\cdot}$ and $RO^{\cdot}$ with the CH_3 groups of the aromatic compounds were detected in the reaction mixtures. The mechanism of the action of element-containing peroxides in the reaction with aromatic derivatives is analogous to the mechanism of the hydroxylation of the latter by organic hydroperoxide (or hydrogen peroxide)—Lewis acid systems, i.e. an electrophilic substitution reaction obtains in the given instance:[13,90,95]



E = B, Si; R = t-C_4H_9 ; R'=CH_3, OCH_3, OC_4H_9.

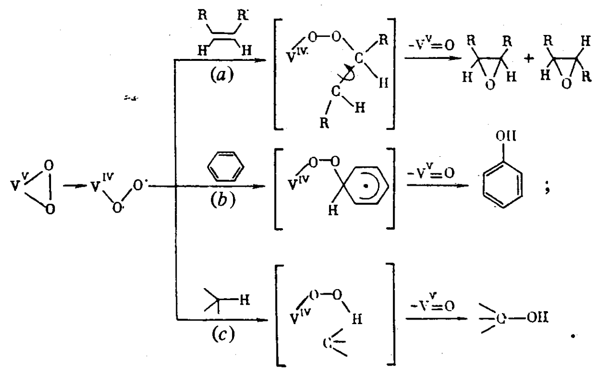
Consequently, in many cases the active oxidising agents in the catalytic autoxidation of organic substances are organoelemental peroxides formed as a result of exchange between the intermediate in the oxidation of hydrocarbons (a hydroperoxide) and the catalytic additive. Alkyl peroxide derivatives of the elements oxidise organic compounds with formation of products whose composition is identical to that obtained using peroxide forms of these elements as the catalyst.[13,76–82,90] The high selectivity of the catalytic oxidation is caused by the interaction of the element peroxides with organic compounds via a molecular mechanism.

The compounds of certain transition elements, used as catalysts of the autoxidation of hydrocarbons, are capable of binding molecular oxygen with formation of peroxo-complexes of the metals.[5,12,96] The peroxide character of the oxygen coordinated to the metal is indicated by IR spectroscopic data for these compounds[5,96] and also by the finding that the peroxo-complexes can be obtained both by the reaction of hydrogen peroxide with derivatives of elements containing the M=O bond[12,97–99] and as a result of the direct interaction of molecular O_2 with the metal complex.[5,12] Furthermore, hydrogen peroxide was evolved in the hydrolysis by strong acids of the adducts of molecular oxygen and palladium and platinum complexes.[12]

Like the alkyl peroxide derivatives of the elements, the peroxo-complexes of metals participate in the catalytic oxidation of saturated hydrocarbons[5,6,11,16–18,99–101] and arenes.[4,99,101] The mechanism of the interaction of the oxygen complex of the metal with the hydrocarbon depends on the nature of the metal complex and the substrate being oxidised; it can be of the free-radical, cryptoradical, or molecular type. The involvement of the peroxo-complexes of metals in the radical-chain oxidation of hydrocarbons, described above (Section II), does not lead to a significant increase of the process selectivity.

The covalent and anionic oxoperoxo-complexes of vanadium(V) of the type $VO(O_2)(O{-}N)L_IL_2$ or $[VO(O_2)(Pic)_2]^-A^+L$ (where O - N = pyridine-2-carboxylate, Pic = picoline-2-carboxylate, L_1, L_2 = H_2O, MeOH, or hexamethylphosphoramide, and A^+ = H^+ or PPh_4^+) in aprotic media under mild conditions, epoxidise olefins and hydroxylate aromatic hydrocarbons to form phenols and hydroxylate alkanes to form alcohols and ketones in yields up to 50, 60, and 25% respectively.[99] The peroxo-complexes of vanadium(V) differ sharply in their reactivities from the analogous molybdenum(VI) compounds.[57,58,86] The vanadium complexes are active only in aprotic solvents, epoxidise olefins non-stereospecifically, and behave as hydroxylating agents. From experimental data, the authors[99] suggested that peroxovanadium(V) complexes are homolytically converted into the reactive V^{IV}–O–$O^{\cdot}$ species in aprotic media. This distinguishes them from the peroxo-complexes of rhodium and molybdenum, investigated elsewhere,[57–60] which interact with olefins via the 1,3-dipolar addition of the fragment M^+–O–O^-.

A cryptoradical mechanism has been suggested[99] for the reaction of peroxovanadium(V) complexes with hydrocarbons:


(8)

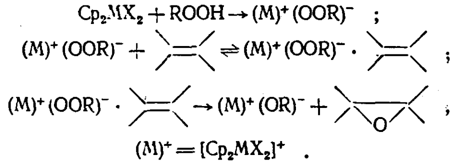
The peroxochromium complex $Ph_3POCrO(O_2)_2$ in the mixed alkane—methylene chloride—t-butyl alcohol solvent oxidises saturated hydrocarbons to alcohols and carbonyl compounds at room temperature. It has been suggested that the mechanism of this reaction is described by an equation analogous to that for pathway (*c*) in Scheme (8).[101] A characteristic feature of the mechanism proposed[99,101] is the combination of the stages involving the reduction of the metal in the peroxo-complex to $M^{(n-1)+}OO^{\cdot}$ and the formation of a new radical species as a result of the interaction of this radical with the olefin or arene [see formula (8), pathways (*a*) and (*b*). In its interaction with the paraffin, $M^{(n-1)+}OO^{\cdot}$ is converted into the metal hydroperoxide $M^{(n-1)+}OOH$ and an alkyl radical [see formula (8), pathway (*c*)]. These intermediate compounds are then oxidised to vanadium(V) or chromium(VI) derivatives and oxygen-containing organic products.

The one-electron oxidation-reduction reactions with participation of the transition metal ion and the hydroperoxide in the catalytic oxidation of hydrocarbons are well known. Furthermore, it has been shown[70] that derivatives of quadrivalent vanadium and t-butyl hydroperoxide, taken in 1 : 1 proportions, react with one another at room temperature to form vanadium(V) compounds. The re-reduction of the latter to vanadium(IV) derivatives under these conditions takes place to an extent not greater than 5%. Consequently, in the oxidation of organic substances by peroxo-complexes of vanadium and chromium, the occurrence of oxidation-reduction reactions of the type $M^{n+} \rightarrow M^{(n-1)+} \rightarrow M^{n+}$ is unlikely.

In our view the oxidation of hydrocarbons by peroxo-complexes of vanadium and chromium with formation of olefin oxides as well as alcohols and phenols probably proceeds without the participation of radicals.

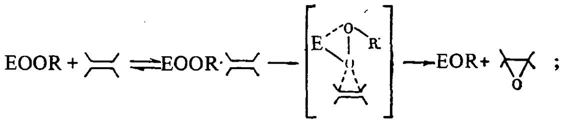
Thus the high selectivity of the catalytic liquid-phase oxidation of organic substances is due to the interaction via a molecular mechanism of the peroxide derivatives of the elements with the C—H bonds of the substrate being oxidised.

(c) *The mechanisms of the interaction of peroxide derivatives of the elements with olefins.* According to Aleksandrov et al.,[71,72] t-butyl hydroperoxide epoxidises olefins at a high rate and with a quantitative yield in the presence of compounds of the type Cp_2MX_2 (where Cp = cyclopentadiene, M = Mo or W, and X = Cl, Br, or I). The epoxidising agent in this process is the metal peroxide formed on oxidation of the initial molybdenum or tungsten compound. The process is described by the scheme:



Alkyl peroxide derivatives of molybdenum of the type $[Cp_2.MoX_2]^+(OOR)^-.ROOH$ have been synthesised by the reaction of biscylopentadienylmolybdenum halides with t-butyl hydroperoxide and their high reactivity in the epoxidation of cyclohexene has been demonstrated.[71]

As stated above (Table 3), the alkyl peroxide derivatives of boron, silicon, and gallium interact with alkenes to form olefin oxides. The alkyl peroxide derivative of the element reacts with the olefin bimolecularly and the epoxidation takes place as a result of the interaction of the electrohpilic peroxide oxygen atom with the π electrons of the double bond in the alkene.[13] The reaction is preceded by the formation of a complex between the reactants:[80,94]

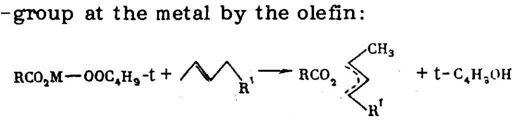


E = B, Si, Ga, Mo, W .

The possibility of the formation of transition states of this type has been confirmed by quantum-chemical calculations.[102,103]

The reactivity of the peroxides of different elements in the epoxidation reaction is determined by the electrophilic character of the peroxide oxygen atoms, which is in its turn related to the acid properties of the heteroatom of the organoelemental compound. The heteroatom, which has an occupied *p* or *d* orbital, interacts with the unshared electron pairs of the peroxide oxygen atoms, which renders the latter more electrophilic and hence more reactive in relation to olefins. There is no information about the electrophilicity of organoelemental peroxides in the literature, but one can postulate that it is correlated with the variation of the acidity of the full oxides of these elements. According to Sheldon and Van Doorn[35] and Tanabe,[104] the properties of the oxides of the elements as Lewis acids weaken in the sequence $MoO_3 \gg Ga_2O_3 > V_2O_5 > B_2O_3 > SnO_2 \gg SiO_2$. The above data for the reactivities of molybdenum, gallium, and boron peroxides in the epoxidation of olefins are consistent with this series. Among the oxides of the elements enumerated, the weakest Lewis acid is SiO_2. Consequently silicon peroxide should not epoxidise olefins effectively. Indeed, on interaction with oct-1-ene, t-butylperoxytributoxysilane forms not more than 0.1 of a mole of octene α-oxide per mole of the peroxide which has reacted, while t-butyl-peroxydibutoxyborane epoxidises oct-1-ene quantitatively under analogous conditions (Table 3).[80]

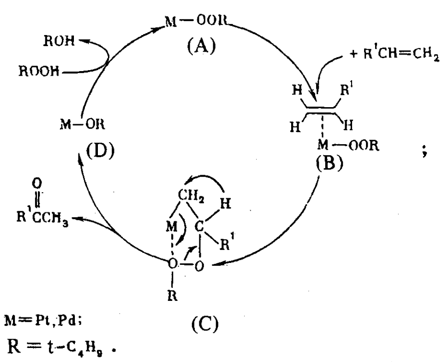
The peroxide derivatives of Group VIIIB elements, whose electrophilic character is weak, convert α-olefins into methyl ketones (Table 3). Thus palladium(II) and platinum(II) t-butylperoxycarboxylates oxidise α-olefins to the corresponding methyl ketones at 20 °C in dry benzene over a period shorter than 10 min (the olefin : peroxide ratio is 50) in 90% yield.[84-86] Aldehydes or other ketones are not formed. β-Olefins are oxidised very slowly or not at all, forming a stable π-allyl complex on substitution of the t-butylperoxy-group at the metal by the olefin:



Platinum(II) t-butyl peroxides of the type *trans*-$(PR_3)Pt(R^1)-OOC_4H_9$-t (where $R_1 = CH_3$, CF_3, or an arene) are also effective in the oxidation of oct-1-ene to 2-octanone (80 °C, 16 h, yield of ketone 80%).[87]

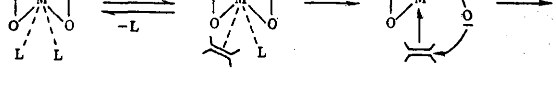
The mechanism of the conversion of α-olefins into ketones by organic peroxide derivatives of palladium and platinum can be represented, according to the authors,[84-87] by a cycle analogous to the catalytic cycle in the hydroperoxide epoxidation of unsaturated compounds in the presence of molybdenum and vanadium derivatives[12] (Scheme III).

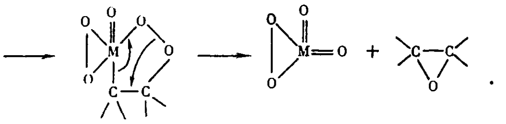
Scheme III



The key stage in this mechanism is the peroxymetallation process, which is preceded by the coordination of the olefin to the metal (B). The intermediate five-membered adduct (C) formed decomposes with cleavage of the O–O bond, which is followed by the β-hydride transfer with formation of methyl ketone and the t-butoxy-derivative of the metal (D). In the presence of an excess of the hydroperoxide, the t-butoxy group is substituted by the t-butylperoxy-group and the initial metal peroxide is regenerated.

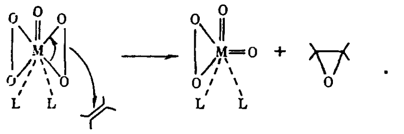
The peroxymetallation process in the epoxidation of olefins and their conversion into ketones by metal peroxo-complexes has been justified in detail.[12,58-60,105-108] The peroxo-complexes of molybdenum and tungsten of the type $L_2MoO(O_2)_3$ (where L are organic ligands with very pronounced electron-donating properties) epoxidise olefins in organic solvents with a high selectivity (the yield of the epoxide can reach 50–90% relative to active oxygen).[58] The reaction takes place in two stages: the reversible coordination of the olefin to the metal is followed by the irreversible transfer of oxygen to the olefin. It is assumed[12] that the oxygen transfer takes place via a cyclic mechanism involving the 1,3-dipolar addition of the peroxo-complex to the olefin with formation of a five-membered metallocyclic compound, which is converted into the epoxide and the dioxo-complex of the metal:



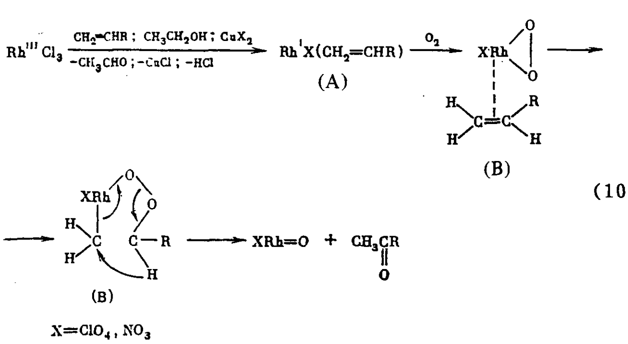

(9)

The exchange of the ligand for the olefin in complexes of this type has been confirmed by analysis of the NMR spectra.[107] Kinetic measurements[105] have shown that the rate of the process is determined by the stage in which the olefin is coordinated to the metal. The results of experiments using the [^{18}O]-labelled peroxomolybdenum complex have shown[106] that exclusively peroxo-oxygen, and not oxo-oxygen atoms as suggested previously,[43] are transferred to the olefin.

A mechanism of the epoxidation of olefins by peroxo-complexes of metals, involving a three-membered transition state, has been proposed[106] as an alternative to Scheme (9):



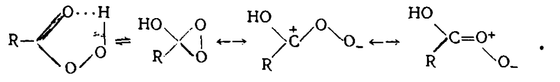
It has been observed[59] that, in the presence of copper perchlorate or nitrate, rhodium complexes in alcoholic solutions at room temperature catalyse the selective conversion of olefins containing the double bond at the end of the carbon chain into methyl ketones on treatment with molecular oxygen. The active species in the reaction, whose mechanism is illustrated in Scheme (10), are olefinic cationic complexes of rhodium (A), capable of activating molecular oxygen with formation of the peroxide complex (B). This compound is converted into the peroxometallocycle (C), which decomposes to the ketone and a rhodium compound containing the Rh=O bond after the migration of the proton to the neighbouring carbon atom:



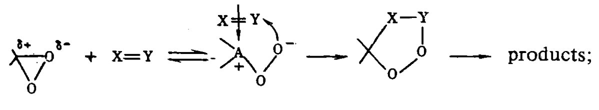
To demonstrate the validity of this mechanism, Igersheim and Mimoun[60] synthesised the peroxorhodium complexes [Rh(As.Ph$_3$)$_4$O$_2$]$^+$A$^-$, where A$^-$ = ClO$_4^-$ or PF$_6^-$, and investigated their interaction with unsaturated compounds. It was found that these complexes react with α-olefins at room temperature in methylene chloride in an atmosphere of argon with formation of methyl ketone, whose yield reached 85%. When the [^{18}O]-labelled peroxorhodium complex is used, methyl ketones containing the labelled oxygen atom in the carbonyl group are formed.[60]

The mechanism represented by Eqns.(9) and (10) requires the coordination of the substrate and an oxygen molecule to one metallic centre. The necessity for the coordination of the olefin is confirmed by the fact that the peroxorhodium complex {RhO$_2$[Ph$_2$P(CH$_2$)$_2$PPh$_2$]$_2$}ClO$_4$, containing two phosphine ligands and not having a free coordination site, is inactive in the reactions with α-olefins.[107] It has been shown[109,110] that the rhodium complex RhCl(C$_8$H$_{14}$)$_2$ with two unsaturated ligands absorbs one mole of oxygen with formation of the peroxo-complex. The coordinated oxygen of the latter oxidises quantitatively the coordinated cyclo-octa-1,5-diene to a ketone at 150 °C in cyclohexene. Furthermore, it has been observed[108,111,112] that oxygen adducts of the type (Ph$_3$P)$_2$ MO$_2$, where M = Ni, Pd, or Pt, in solutions in methylene chloride readily combine with electrophilic olefins. This results in the formation of stable peroxometallocycles in a high yield. It has been demonstrated by NMR and IR spectroscopy that these products are analogous to those formed in accordance with Scheme (10).[61,105,107]

It has been suggested that dioxirans are reactive intermediates in the oxidative reactions of olefins on treatment with oxygen, ozone, and hydroperoxides with participation of catalysts (compounds of different elements and also peroxyacids).[112] The formation of dioxiran, present in the form of a stable zwitterion in the case of peroxyacids, has been confirmed by indirect data:[112]



The transfer of oxygen to organic substrates takes place in two stages. A charge-transfer complex between the nucleophilic substrate (for example, the olefin) and the electrophilic carbon atom of the dioxiran or the metal of the peroxo-complex is formed initially in the slow reversible stage. In the second stage, the coordinated substrate adds to the nucleophilic terminal oxygen atom and a cyclic peroxide is formed and then decomposes to the corresponding products:



A = carbon, metal.

Thus the catalytic reactions involving the oxidation of unsaturated compounds by oxygen and hydroperoxides take place via a non-radical mechanism and with a high selectivity. The peroxide derivatives of the elements—alkyl peroxides and peroxo-complexes—play an active role in these reactions. The interaction of the peroxide derivative of the element with the olefin takes place via intermolecular nucleophilic attack by the peroxide oxygen atom, coordinated to the organoelemental compound of the alkene. There is no unanimous view concerning the structures of the transition states in this process. The nature and yield of the products of the oxidation of the unsaturated compound and also the activity of the peroxide derivative of the element in its reaction with the olefin are determined by the electron-accepting properties of the heteroatom in the organoelemental compound.

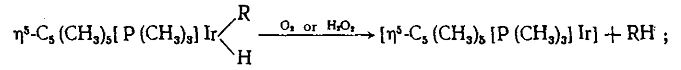
IV. CONCLUSION

An increase in the selectivity of the liquid-phase oxidation of organic compounds by molecular oxygen can be achieved by employing compounds of different elements as catalysts. The multiplicity of the catalytic system is responsible for the absence of a single mechanism of the catalytic oxidation of hydrocarbons. However, it has been established firmly that the selectivity of the oxidation of organic compounds increases when the process proceeds without the participation of free radicals and the obligatory activation of the oxidant. The oxidant is in many cases activated as a result of the formation of peroxides of different types, which accumulate in the reaction mixture as a consequence of the addition of oxygen to the metal complex or the exchange between the primary oxidation product (hydroperoxide) and the ligands of the catalytic additive. The peroxo-complex or the alkyl peroxide derivative of the element interact with the organic substance by a molecular mechanism, effecting with a high selectivity the direct transfer of oxygen to the hydrocarbon.

The activation of the substrate as a consequence of its coordination to the catalyst in selective catalytic oxidation reactions of organic substances has been reliably demonstrated for unsaturated and aromatic hydrocarbons. However, the necessity for the activation of the C–H bonds of alkanes in their selective oxidation needs experimental confirmation. According to Shilov and Shteinman,[113,114] in homogeneous systems alkanes can be activated by their oxidative addition to a transition metal complex.

Since the discovery of the activation of alkanes in aqueous solutions of platinum(II) complexes by Shilov and co-workers,[115] numerous examples of the activation of the C–H bonds of paraffins by iridium, rhodium, ruthenium, and rhenium compounds[116–119] and also by complexes of the type of the Ziegler–Natta catalyst[120] have been discovered. However, hitherto such activation has not been observed in autoxidation processes. On the contrary, there exist data which permit the claim that the activation of the alkane via its oxidative addition to the transition metal complex is not an essential condition for the selective conversion of the substrate into an oxygen-containing product.

Thus it is known that iridium compounds of the type IrX.(CO)PPh$_3$, where X = Cl or Br, activate the O_2 molecule with formation of the peroxocomplex and catalyse the autoxidation of ethylbenzene to acetophenone and of *p*-xylene to *p*-toluic aldehyde.[4] It has been shown recently that the iridium complex η^5-$C_5(CH_3)_5[P(CH_3)_3]Ir(H_2)$ activates alkanes and arenes with formation of hydridoaryl and hydridoalkyl derivatives of iridium.[119] However, treatment of the compounds obtained with oxygen or hydrogen peroxide leads only to the reductive elimination of the unchanged hydrocarbon molecule:



$$\eta^5\text{-}C_5(CH_3)_5[P(CH_3)_3]Ir\begin{matrix}R\\H\end{matrix} \xrightarrow{O_2 \text{ or } H_2O_2} [\eta^5\text{-}C_5(CH_3)_5[P(CH_3)_3]Ir] + RH\,;$$

$$R{=}CH_3,\ CH_2C(CH_3)_3,\ C_6H_{11},\ C_6H_5\ .$$

Furthermore, in the selective oxidation of hydrocarbons by the alkyl peroxide derivatives of non-transition elements (boron, aluminium, silicon, etc.), it is difficult to imagine that the alkanes are activated as a result of oxidative addition.

Consequently, the decisive factor in this process is the activation of the oxidant. The high selectivity of the oxidation of organic substances with participation of peroxide derivatives of the elements is caused, from our point of view, by the special state of the peroxide bond in the alkyl peroxide or peroxo-complex molecule "activated" by the heteroelement. Thus the activation of the O–O bond can lead to the formation of the oxiran ring, which facilitates the electrophilic attack by the peroxide oxygen on the nucleophilic organic substrate[112] or promotes the molecular interaction of the peroxide with the C–H bonds of the substance oxidised, which proceeds in a cyclic activated state.[113]

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Arenechromium Tricarbonyls in Organic Synthesis

V.N.Kalinin

The characteristic features of the chemical properties of arenechromium tricarbonyls, caused by the change in the reactivity of the aromatic groups and the organic substituents linked to them on passing from ArH to $ArHCr(CO)_3$, are examined and data concerning the application of arenechromium tricarbonyls in organic synthesis are surveyed.
The bibliography includes 167 references.

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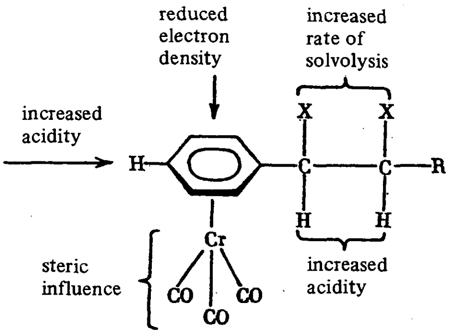
I. INTRODUCTION

The present stage in the development of organic synthesis is characterised by the wide-scale application of organoelemental and organometallic reagents in order to effect chemoselective, regioselective, and stereoselective processes, which are frequently impossible within the framework of the usual "organic" scheme. During the last 15–20 years, transition metal complexes (TMC) have been vigorously employed in organic synthesis together with traditional derivatives of non-transition metals (Grignard reagents, lithium alkyls), etc.). It is possible to differentiate two main aspects of the application of TMC in synthesis—catalytic reactions and reactions in stoichiometric proportions. The latter presuppose the existence of three stages: (a) the formation of a complex between the organic substrate and the transition metal (TM); (b) the use of the characteristic features introduced by the TM for the chemical modification of the organic residue; (c) decomposition of the complex and isolation of the altered organic molecule. For the effective employment of TMC in synthesis, these stages must proceed with high yields and the complex itself must be cheap and readily available. These requirements are to a large extent satisfied by derivatives of benzenechromiumtricarbonyl (benchrotrene),[†] which are readily obtained from organic derivatives and $Cr(CO)_6$ or $L_3Cr(CO)_3$ (L = Py, MeCN, or NH_3).

The synthesis of BCT has been examined in detail in various chapters of existing monographs.[1-3] The preparative method has been described specifically in two communications.[4,5] The physicochemical properties of BCT, the nature of the bonding in these compounds, and the principal factors influencing the orientation of the ChTC relative to the arene ligand have been discussed in a review.[6] The reactivity of BCT and their applications in organic synthesis in individual stages have been described in monographs,[7,8] and in greater detail in reviews.[9-14] Striking examples of the employment of BCT in synthesis have been published recently.

The present review deals both with studies having a bearing on specific applications in organic synthesis and studies of the reactivity of BCT which may find applications in the future. The ligand exchange reactions of BCT and the metallotropic rearrangements in a series of condensed systems containing ChTC will not be discussed. Earlier studies included in previous reviews[6,12] are quoted whenever necessary and in a more concise form.



The influence of the formation of a complex with ChTC on the reactivity of the arene ligand.[10]

The formation of a complex between the arene ligand and ChTC imposes characteristic features on the reactivity of the ligand. The changes in the properties of the ligand and the groups linked to it are illustrated in the Figure.[10] The introduction of ChTC leads to strong withdrawal of electron density from the arene ligand (the electron-accepting effect of ChTC is comparable to the influence of the nitro-group),

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[†] The following notation has been adopted in the text of this review: BCT = benchrotrene $(PhH)Cr(CO_3)$ and its ring-substituted derivatives $(Arene)Cr(CO)_3$ also the benchrotrenyl residues $(CO)_3Cr(Ph^-)$; ChTC or [Cr] = $Cr(CO)_3$ group.

which is manifested by the high acidity of the ChTC derivatives of benzoic acids,[15,16] phenols,[17] and anilinium ions[18] compared with the corresponding benzene compounds.

The ability of the aromatic system to transmit the electronic effect of the substituent is significantly reduced in BCT.[16] The correlation of the thermodynamic dissociation constants of 38 substituted ChTC-benzoic acids in 50% aqueous ethanol at 25 °C within the framework of the Yukawa–Tsuno equation showed that the reaction constant ($\rho = 0.8$) is significantly lower than for benzoic acids ($\rho = 1.4$).

The complex formation reaction between the arene and ChTC promotes the stabilisation of α-carbenium ions and to some extent also β-carbenium ions, increases the acidity of the C–H bonds in the arene ligand and in the α-position in an alkyl substituent, and facilitates nucleophilic addition and substitution reactions. ChTC exerts an appreciable steric influence on the reactions of BCT. These effects are used in synthesis.

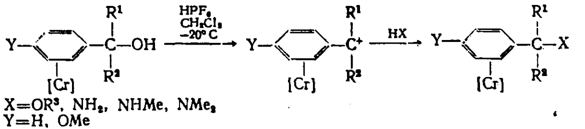
Arenes are usually isolated from BCT by oxidation with iodine[15] or cerium(IV) salts,[19] exposure to light,[20] or displacement with *n*-donor ligands: amines[21] and phosphines.[22]

II. REACTIONS PROCEEDING VIA α-CARBENIUM IONS

A characteristic feature of the BCT substituent, and in general of metallocenyl substituents,[23] is its great ability to stabilise the carbenium centres in the α-position relative to the aromatic ligand. This is indicated by the high rates of solvolysis of $(PhCH_2Cl)ChTC$ and $(Ph_2CHCl)ChTC$ in 80% aqueous acetone, amounting to 2.2×10^{-4} s^{-1} and 7.0×10^{-2} s^{-1}, which is respectively 10^5 and 10^3 times higher than the rate of solvolysis of benzyl chloride and diphenylmethyl chloride.[24] These kinetic results are in good agreement with the thermodynamic stability constants of the carbenium ions:[25] $pK_{R^+} = -11.8$ for $(\pi\text{-}PhCH_2^+)ChTC$, $pK_{R^+} < -17.3$ for $PhCl_2^+$, and $pK_{R^+} = -13.4$ for Ph_2CH^+.

The formation of complexes with ChTC appreciably increases the rate of isomerisation of benzyl thiocyanate to benzyl isothiocyanate $[(PhCH_2SCN)ChTC \rightarrow (PhCH_2NCS)ChTC]$;[26] the rate-determining stage of the process is ionisation.

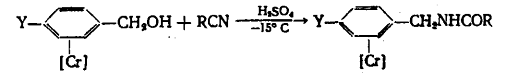
The formation of complexes by benzyl alcohols with ChTC and the subsequent generation of carbenium ions lead to extensive possibilities for the synthesis of *N*- and *O*-benzyl derivatives. The reactions of ChTC-containing carbenium ions with NH_3, amines, and alcohols provide convenient methods of synthesis of the corresponding derivatives:[27]



$X = OR^3, NH_2, NHMe, NMe_2$
$Y = H, OMe$
$R^1, R^2 = H, Me, Ph$
$R^3 = Me, Et$

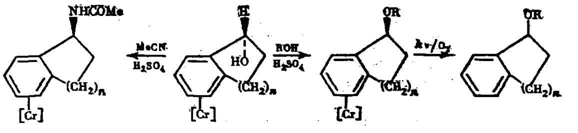
This approach greatly expanded the range of alcohols used in the Ritter reaction. Tertiary alcohols usually afford satisfactory yields of amides in this reaction, while the use of primary and secondary alcohols leads to unsatisfactory results.

The primary BCT-carbinols react smoothly with various nitriles, forming *N*-benzylamide complexes:[28,29]



$Y = H, OMe$
$R = Me, Pr, Ph, o\text{-}MeC_6H_4, PhCH_2, ClCH_2, CH_2{=}CH$

The formation of complexes with ChTC imparts characteristic features to the stereochemical course of the reactions of the intermediate carbenium ions. This is clearly illustrated by the total stereospecificity of the reactions of the carbenium ions generated from (*endo*-1-indanol)ChTC (I) and (*endo*-1-tetralinol)ChTC (II): the reactions with H_2O, MeOH, and RCN are accompanied by the complete inversion of configuration and the formation of *exo*-products:[29–31]

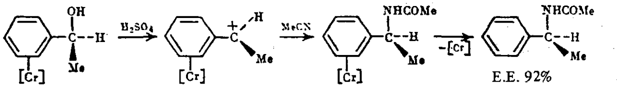


(I), (II)

R = H, Me; *n* = 1 (I), 2 (II)

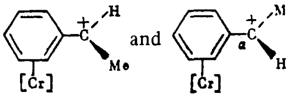
The racemisation of optically active complexes is not observed in these reactions and the photochemical decomposition of the complexes also proceeds with almost 100% retention of configuration.

Even in the acyclic series the reaction of BCT-carbinols via carbenium ions proceeds with an appreciably stereoselectivity.[29,32] The high degree of retention of optical purity in the products formed has been demonstrated in relation to the reactions of optically active *S*-(+)-(α-hydroxyethylbenzene)-ChTC, for example:



E.E. = enantiomeric excess.

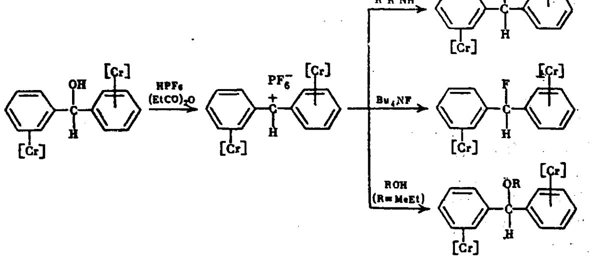
The retention of configuration in acyclic systems can be explained by *exo*-attack in the formation of the carbenium ion and in its subsequent reactions, i.e. of the two potentially feasible carbenium ions (A) and (B), namely



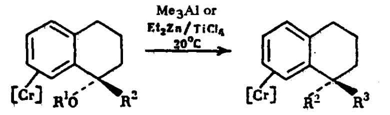
(A) (B)

the ion (A) is formed and the interconversions (A) ⇌ (B) are hindered by the high energy barrier to the rotation about the C(1)–C(α) bond.[33]

The stable α-carbenium ions with two ChTC, isolated in the solid crystalline state, are of special interest.[34,35] They are formed in the reaction of doubly complexed diphenylmethanol in propionic anhydride with 55% HPF_6. On treatment with alcohols, these complexes give rise to esters, while their reactions with primary and secondary amines afford secondary and tertiary amines respectively. Reactive aromatic substrates, namely dimethylaniline, pyrrole, and *N*-methylpyrrole are alkylated by carbenium ions but anisole and less nucleophilic aromatic derivatives do not react with them.[34,45] The reaction with tetrabutylammonium fluoride yielded the corresponding π-complex of diphenylmethyl fluoride:[27]

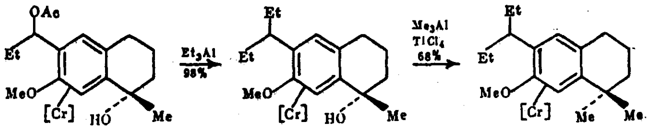


The ChTC-derivatives of *endo*-benzyl alcohols and their acetates are convenient sources of alkyl derivatives, which are obtained by reaction with Me_3Al or Et_2Zn in the presence of $TiCl_4$:[36]

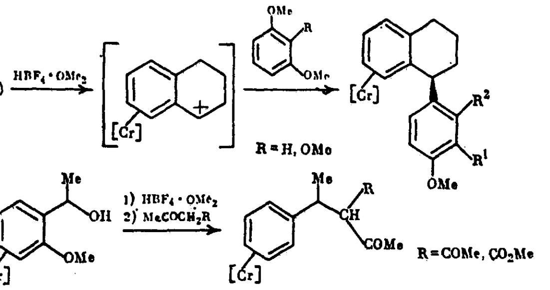


$R^1=H$, Ac; $R^2=H$, Me; $R^3=Me$, Et

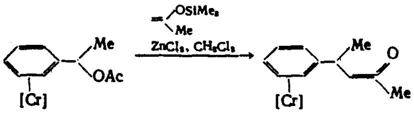
Depending on the conditions, when the substrate contains two types of benzyl hydroxy-groups, it is possible to introduce stepwise different alkyl groups:



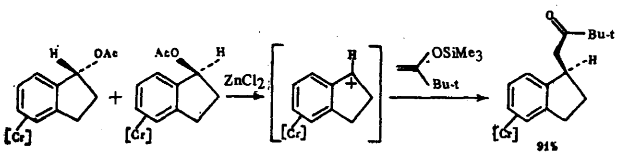
The BCT-carbenium ion, formed *in situ*, reacts rapidly with aromatic derivatives containing electron-donating groups and with β-dicarbonyl compounds, forming *exo*-substituted complexes:[37]



The acetates of α-BCT-carbinols are active alkylating agents and produce ketones smoothly in reactions with silyl enol ethers,[38] for example:



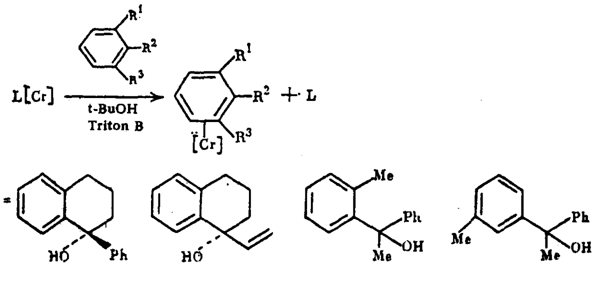
The reaction of a distereoisomeric mixture of indanyl acetates, bound in a complex, with 1-t-butyl-1-trimethylsiloxyethylene leads to a single *exo*-substituted complex via an intermediate carbonium ion with planar chirality:



The alkylation of enol ethers by the acetates of α-BCT-carbinols provides a convenient preparative method for the stereospecific formation of a C–C bond.

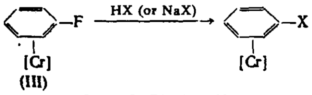
It is noteworthy that it has been suggested that BCT with t-hydroxy-groups in the ligand, which exhibit an increased tendency towards the formation of carbenium ions, be employed for the transfer of ChTC to other arenes.[39,40]

The reaction is used for the synthesis of BCT with functional-group substituents:



III. NUCLEOPHILIC SUBSTITUTION AND ADDITION

The strong electron-accepting effect of ChTC facilitates reactions involving nucleophilic substitution in (η^6-halogenoarene)ChTC. The fluorine and chlorine atoms in BCT are readily substituted by *O*-, *S*-, and *N*-nucleophiles, the fluorobenzene complex (III) exhibiting the highest reactivity:[41–44,75]:



(III)

X=RO, RS, RNH, R_2N

The relative ease of substitution of the halogen by the MeO group in halogenobenzenes activated by complex formation increases in the following sequence for different π-linked organometallic residues:[45,46]

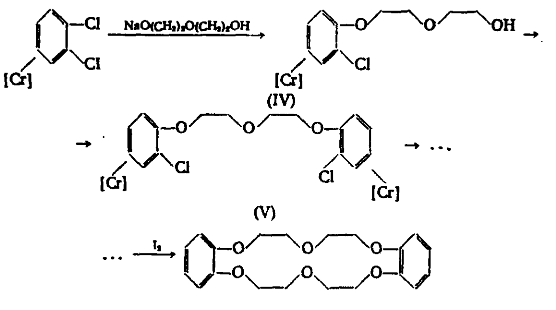
$$(OC)_3Cr < (OC)_3Mo < (\eta^5\text{-}C_5H_5)Fe^+ < (OC)_3Mn^+$$

Difluoro-BCT readily exchanges both fluorine atoms for methoxy-groups.[47]

The halogen in (halogenbenzene)ChTC is readily exchanged for the mercapto-group under the condition of phase-transfer catalysis.[48]

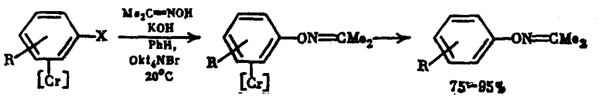
In (dichlorobenzene)ChTC, the substitution of the halogens can be carried out consecutively.[49,50]

The possibility of the stepwise substitution of chlorine atoms in (1,2-dichlorobenzene)ChTC permitted its use in the synthesis of dibenzo-18-crown-6 ether by reaction with the sodium salt of diethylene glycol via the complexes (IV) and (V):[51]



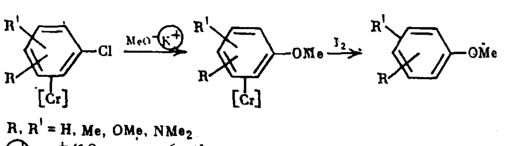
The yield of the crown ether is 27%.

Under the conditions of phase-transfer catalysis, BCT reacts smoothly with acetone oxime, forming *O*-aryloximes:[52]



R = H, *o*-Me, *m*-Me, *p*-Me; X = Cl, F.

when (chloroarene)ChTC is heated with non-solvated MeOK in benzene or acetonitrile in the presence of 18-crown-6 ether, (methoxyarene)TC is formed in high yields:[53]



R, R' = H, Me, OMe, NMe$_2$
K⁺ = K$^+$/18-crown-6 ether

Intramolecular nucleophilic substitution in the series of BCT is an effective method of synthesis of benzocyclic systems, for example, chromans:[54,55]

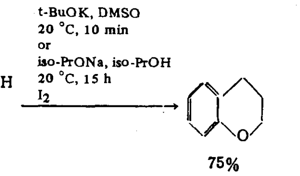
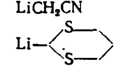
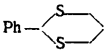
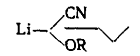
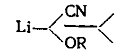
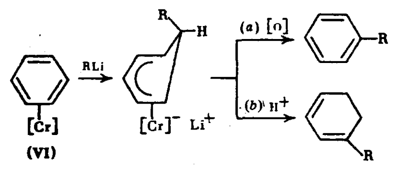


Table 1. The coupling of carbanions to BCT [Eqn.(1a)].[10,56]

Carbanion	Product	Yield, %
LiCMe$_2$CN	PhCMe$_2$CN	94
LiCH$_2$CN	PhCH$_2$CN	68
		93
	PhCO(CH$_2$)$_2$Me	90*
	PhCOPr-iso	88*
LiCH(SPh)$_2$	PhCH(SPh)$_2$	84
LiBu-t	PhBu-t	97
		71
LiCH$_2$CO$_2$Bu-t	PhCH$_2$CO$_2$Bu-t	87
LiCHMeCO$_2$Bu-t	PhCHMeCO$_2$Bu-t	88
LiCMe$_2$CO$_2$Bu-t	PhCMe$_2$CO$_2$Bu-t	88

*R = CHMeOEt; the products were isolated by successive acid and base hydrolysis.

A notable property of *C*-nucleophiles is their ability to add to BCT with formation of η^5-cyclohexadienyl complexes, which are formal analogues of Meisenheimer complexes.[56] The reaction takes place rapidly at 0 °C. It has been shown from the products of the addition of the lithiodithiane complex to BCT that the entering substituent occupies the *exo*-position in the structure, where one of the ring carbon atoms is deflected in the opposite direction relative to ChTC.[57] Anionic complexes are capable of two types of reactions:

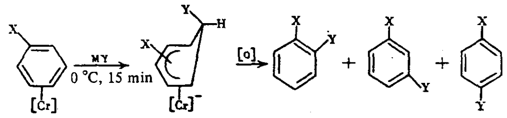
 (1)

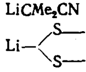
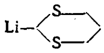
(VI)

The oxidation of the complex leads to the formal substitution of the hydride ion by the carbanion (pathway *a*) and the formation of a substituted benzene. The process has come to be called "addition/oxidation".[56,58] The protonation of the complex by strong acid liberates alkylcyclohexa-1,3-diene ("addition/protonation", pathway *b*).[56,59,60] "Addition/oxidation" has potentially many applications in organic synthesis for the phenylation of organic compounds (Table 1).[10,56]

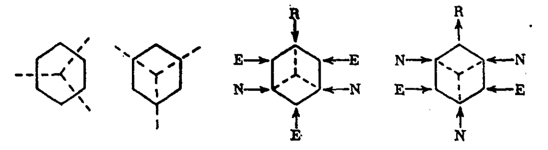
Reactive organolithium compounds are effectively phenylated by BCT under mild conditions in tetrahydrofuran (THF).

Table 2. The mode of addition of carbanions to BCT.[61,62]

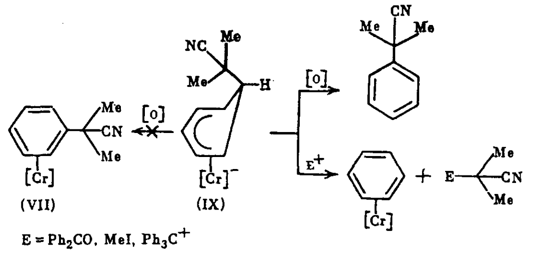


X	MY	Product ratios *o*:*m*:*p*
Me	LiCH$_2$CO$_2$Bu-t	28:72:0
Me	LiCMe$_2$CO$_2$Bu-t	3:97:0
Me	LiCMe$_2$CN	1:97:2
Me		51:47:2
OMe	LiCH$_2$CO$_2$Bu-t	4:96:0
Cl	LiCH$_2$CO$_2$Bu-t	54:45:1
Cl	LiCHMeCO$_2$Bu-t	53:46:1
Cl	LiCMe$_2$CO$_2$Bu-t	5:95:1
Cl	LiCH$_2$COBu-t	76:24:0
Cl	LiCMe$_2$CN	10:89:1
Cl		46:53:1
SiMe$_3$	LiCMe$_2$CN	0:2:98
CF$_3$	LiC(CN)(OR)Me	0:30:70
NMe$_2$	LiCMe$_2$CN	1:99:0
Et	LiC(CN)(OR)Me	0:94:6
iso-Pr	LiC(CN)(OR)Me	0:80:20
t-Bu	LiC(CN)(OR)Me	0:35:65
CH(Bu-t)$_2$	LiC(CN)(OR)Me	0:0:100

In substituted BCT the nature of the substituent has a decisive influence on the regioselectivity of the addition of nucleophiles (Table 2).[61,62] To a lesser extent the ratio of the isomers is influenced by the nature of the nucleophiles. The direction of attack by the reactants on BCT is qualitatively correlated with the coefficients of the lowest unoccupied molecular orbital of the free arene, which is associated with the distribution of charge density, and attack by the nucleophiles Nu is directed preferentially to the carbon atom eclipsed by the CO group, while that of the electrophile E is directed to neighbouring atoms.[63–66] Despite the low energy barrier between the hindered (C) and eclipsed (D) conformations (~0.3 kcal mol^{-1}), BCT's with an electron-donating substituent exist preferentially in the *syn*-eclipsed conformation (E), while those with an electron-accepting substituent exist in the *anti*-eclipsed conformation (F):

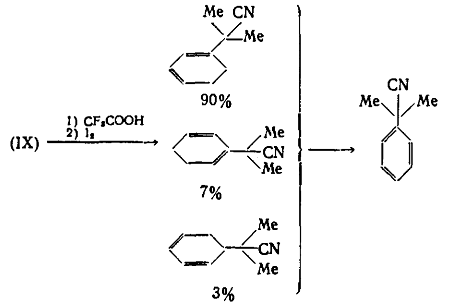


Nucleophilic substitution takes place in the *m*-position in complexes with R = OMe or NMe$_2$ and in the *p*-position in those with R = CF$_3$ or SiMe$_3$. Alkyl-BCT are an exception.[67] With increase of the bulk of the alkyl group, *p*-attack become preferred to *m*-attack. The attempts to obtain the complex (VII) by the selective oxidation of the adduct (IX), obtained by the reaction of the BCT with 2-lithio-2-methylpropionitrile (VIII) on treatment with I_2, $FeCl_3$, benzoquinone, $CuCl_2$/DMF,# and cerium(IV), led only to the formation of 2-methyl-2-phenylpropionitrile. When electrophiles are used as hydride ion acceptors, the initial arene complex is regenerated as a consequence of the abstraction of the carbanion:[56,57]

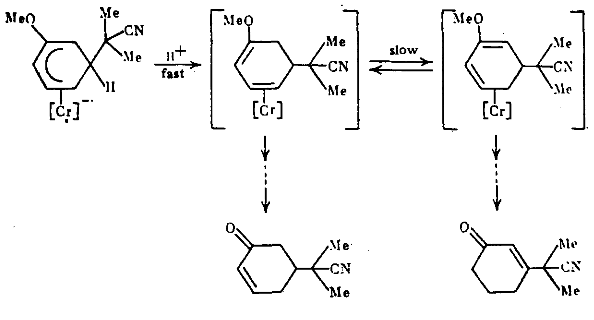


E = Ph_2CO, MeI, Ph_3C^+

The intermediate (IX) reacts rapidly with proton donors (H_2O, AcOH, CF_3CH_2OH) to regenerate the initial BCT in 70—90% yield, while on treatment with CF_3COOH (5 equiv.) and subsequent oxidation a mixture of isomeric cyclohexadienes is formed and can be readily aromatised:[57]

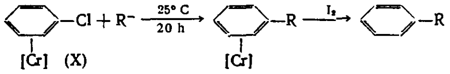


In the case of the adduct of (η^6-anisole)ChTC and compound (VIII), proton transfer results in the formation of dienol ethers, whose hydrolysis affords 3- and 5-substituted cyclohexenones; the ratio of the latter depends on the duration of stirring with acid:



If the adducts of nucleophiles with BCT are treated with CF_3COOH in an atmosphere of CO, then $Cr(CO)_6$ is readily regenerated together with dienes or arenes.[68]

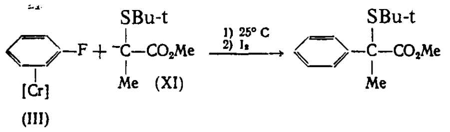
The reaction involving nucleophilic substitution of chlorine in (η^6-chlorobenzene)ChTC by stabilised carbanions, which can be regarded as a preparative phenylation method, has been discovered:[69,70]



R=CMe_2CN, CMe_2CO_2Et, $CMe_2CO_2^-$, $CH(CO_2Et)_2$, C(Ph)(CN)(OCHMeOEt)

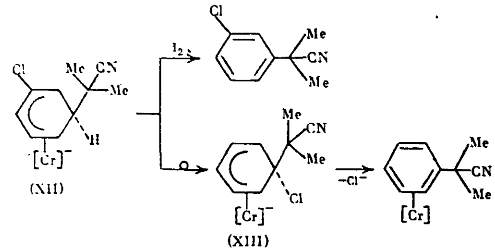
The lithio-derivatives of 1,3-dithiane, 2-methyl-1,3-dithiane, t-butyl acetate, acetophenone, 5,6-dihydro-2,4,4,6-tetramethyl-4*H*-1,3-oxazine, and acetonitrile are not phenylated under these conditions. Primary and secondary carbanions are apparently relatively ineffective in this reaction owing to the presence of an active hydrogen atom. The diethylmalonate anion, which reacts slowly with the complex (X), is an exception.

It has been shown that the fluorine-containing complex (III) reacts rapidly with the carbanion (XI), giving rise to methyl α-(t-butylthio)-α-phenylpropionate in 94% yield after the decomposition of the complex:

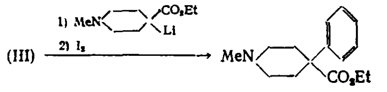


The rate of nucleophilic substitution of the halogen in (η^6-halogenobenzene)ChTC depends on the character of the leaving group and diminishes in the sequence F > Cl > I.[70]

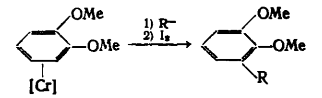
The mechanism of the nucleophilic substitution of the halogen in halogeno-BCT is complex. For example, when (chlorobenzene)ChTC (X) is treated with 2-lithio-2-methylproprionitrile (VIII) at −78 °C and is then oxidised, a 1,3-disubstituted benzene is formed. However, at 20 °C the intermediate (XII) slowly isomerises to the complex (XIII), which loses Cl^- and gives rise to an *unco*-substitution product:[56]



Nucleophilic substitution and addition reactions have found applications in fine organic synthesis. Thus substitution of the fluorine atom in (PhF)ChTC (III) by the carbanion derived from 4-ethoxycarbonyl-1-methylpiperidine leads to the analgesic demirol in 85% yield:[56]

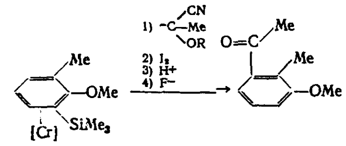


The regioselectivity of the nucleophilic attack has been used in the synthesis of polysubstituted benzenes. The role of the MeO and Me_3Si groups as *m*- and *p*-directing groups respectively is a decisive factor in the synthesis of 1,2,3- and 1,2,4-trisubstituted benzenes:[62]

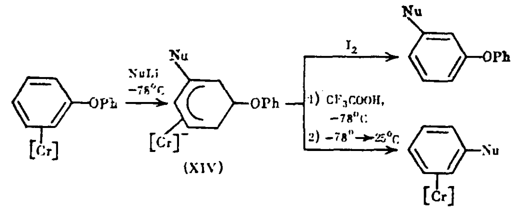


R=CH_2CN, CMe_2CN

DMF = dimethylformamide.

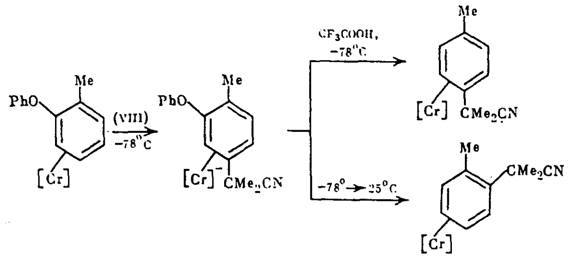


It has been shown[71] that (diphenylether)ChTC reacts with stabilised carbanions to form *m*-substituted diphenyl ethers after oxidation. If the anionic complex (XIV) is treated with CF_3COOH at −78 °C or is heated to room temperature, then the product of the substitution of the PhO group by the nucleophile is formed:

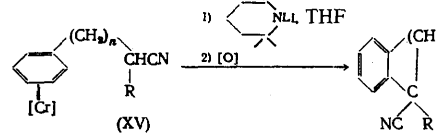


Nu = CH_2CN, CHMeCN, CMe_2CN, $CHMeCO_2Bu$-t, C(Ph)—S—$(CH_2)_3$—S

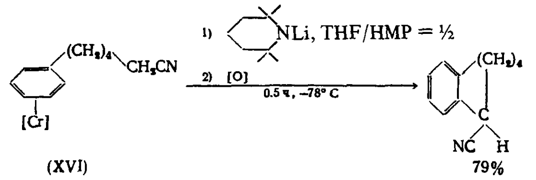
The high regioselectivity of the substitution of the phenoxy-group has been established for the reaction of (*o*-phenoxytoluene)ChTC with compound (VIII): treatment with CF_3COOH leads to a p-disubstituted complex, while heating to room temperature affords the *o*-disubstituted complex:



The nature of the product formed has been investigated as a function of the number of methylene units separating the aromatic ligand and the CN group for systems capable of intramolecular addition.[72] 1-Cyanotetralin is formed from the complex (XV, *n* = 3);

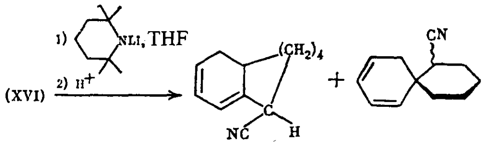


When *n* = 4, the position where the nucleophile adds depends on the reaction time and temperature:

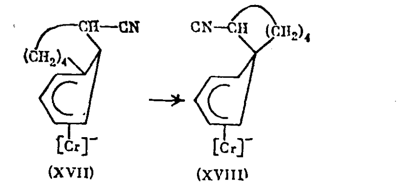


With increase of temperature and of the reaction time, the fraction of high-molecular-weight products also increases.

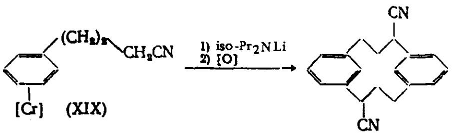
High yields of monomeric products are retained under protonation conditions, but their ratio also depends on the reaction time and temperature. For example, the amounts of condensed and spiro-products at 0 °C are 25 and 75% after 4 h and 3 and 97% respectively after 24 h:



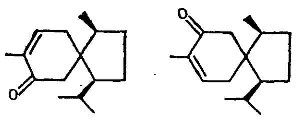
The most rational explanation involves the initial formation of compound (XVII) as the kinetically controlling product; a 1,2-carbon shift converts this adduct into the thermodynamically more favourable complex (XVIII):



For low homologues (XIX, *n* = 2), the formation of both spirocyclic and condensed products is favourable, so that dimeric compounds are formed:

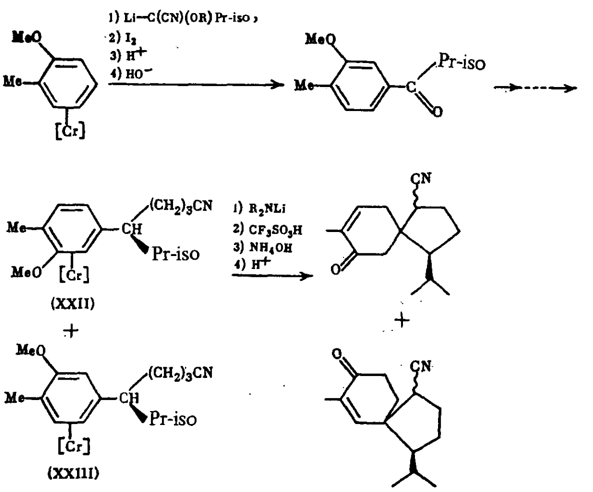


The characteristic features of the addition of nucleophiles have been used in the synthesis of spiro[4.5]decane system—acorenone (XX) and acorenone B (XXI):[14]



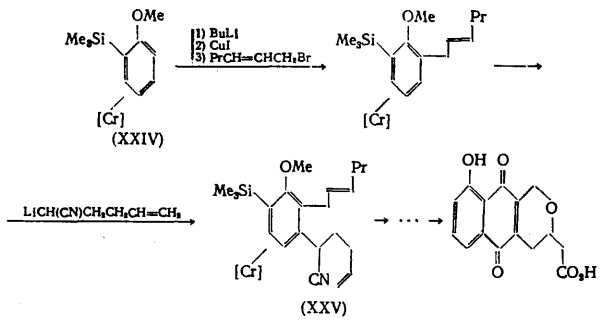
(XX) (XXI)

The strategy used in the synthesis is based on the *m*-directing effect of the methoxy-group in the nucleophilic addition to the anisole complex; *exo*-attack is then controlled by the configuration of the spiro-carbon:



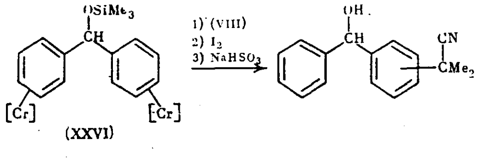
The diastereoisomeric mixture of the complexes (XXII) and (XXIII) was separated by preparative liquid chromatography; the low efficiency of the spirocyclisation complexes vitiates the prepartive importance of this synthesis.

Complex formation with ChTC has been a convenient method of preparation of synthons on the way from frenolicin to deoxyfrenolicin—antibiotics based on the isochromanquinone skeleton.[74] The fundamental factor is the use in the initial stages of the *p*-directing effect of the Me_3Si group and the *m*-directing effect of the MeO group in the nucleophilic addition of the complex (XXIV); this results in the selective formation of compound (XXV), from which the Me_3Si group can be readily removed. It is noteworthy that the lithio-derivative of the complex (XXIV) does not react directly with 2-hexenyl bromide and was therefore converted into an organocopper derivative:

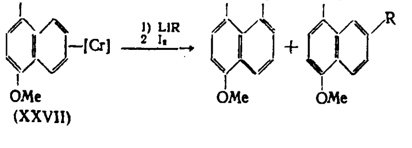


The overall yield of deoxyfrenolicin is 4% after a 15-stage synthesis.

The decisive role of the conformation of ChTC in the mode of nucleophilic attack on the BCT has been confirmed.[75] The reaction of 2-lithio-2-methylpropionitrile with the complex (XXVI), for which the *syn*-eclipsed conformation is characteristic, and subsequent oxidation yielded a mixture of monosubstituted diphenylmethanols with the ratio $m/p = 9/1$:

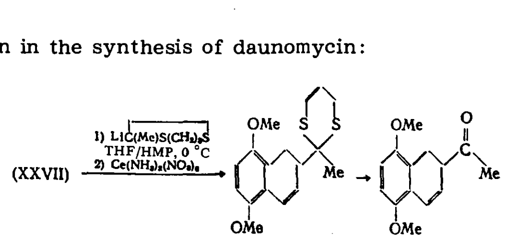


The addition of nucleophiles to polycyclic aromatic complexes is of considerable interest. In this case the steric requirements of the arene substituent and the nucleophile have a marked influence on the regioselectivity of the nucleophilic attack together with the conformational effect and the nature of the substituent in the nucleus.[76] The reaction of the small $LiCH_2CN$ molecule with the complex (XXVII) affords mainly the α-substitution product, while the more bulky compound (VIII) gives rise to the β-substitution product:

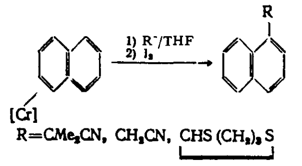


Depending on the reaction time and temperature, different ratios of the α- and β-products are observed and the β-addition product rearranges via dissociation with elimination of a carbanion to the thermodynamically favourable α-addition product.

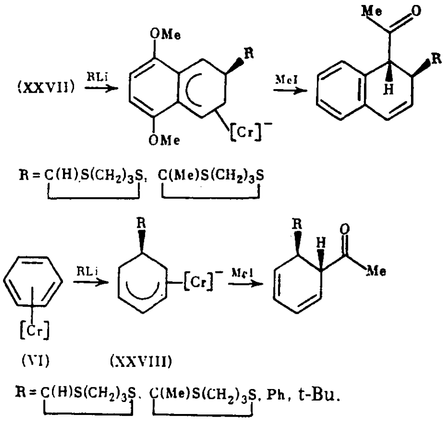
In the case of 2-lithio-2-methyl-1,3-dithiane, the β-addition is irreversible and this reaction has been used to synthesise 6-acetyl-1,4-dimethoxy-5,6-dihydronaphthalene—the synthon in the synthesis of daunomycin:



However, carbanions add to (naphthalene)ChTC in the α-position:

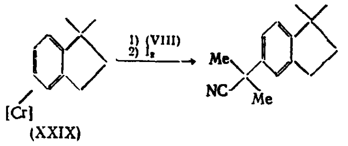


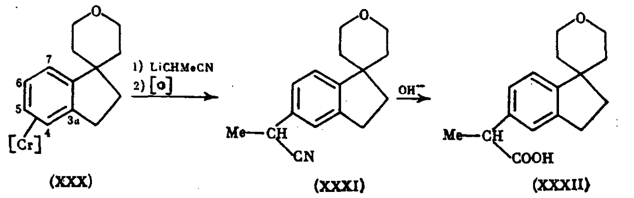
The ability of *S*-stabilised carbanions to add irreversibly to BCT with formation of anionic complexes, which react with electrophiles (MeI), is the basis of a general method of synthesis of disubstituted dihydronaphthalenes and cyclohexadienes:[78]



The insertion of CO has been observed when the reaction was carried out both in an atmosphere of carbon monoxide and in its absence. Other electrophiles also proved to be effective in the synthesis of 5,6-disubstituted cyclohexa-1,3-dienes.[9]

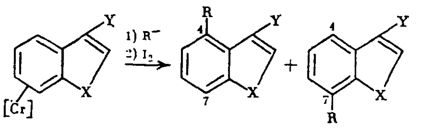
The ability of nucleophiles to add preferentially to the eclipsed carbon atoms of the arene liquid is manifested strikingly in the reactions of 1,1-disubstituted indan complexes.[66,80] The reactions of cyano-stabilised carbanions with the complexes (XXIX) and (XXX) and subsequent oxidation lead to 5-substituted indans:



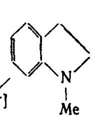


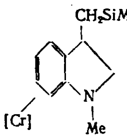
Hydrolysis of compound (XXXI) affords the pharmacologically valuable 5-substituted acid (XXXII). According to the results of X-ray diffraction analysis of the complex (XXX),[80] the CO groups are in the eclipsed conformation relative to the 3a, 5-, and 7-positions in the arene ligand.

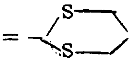
The method involving the addition/oxidation of reactive *C*-nucleophiles to BCT has been extended to complexes of *N*-substituted indoles, *N*-methylindoline, and benzofuran.[81,82] The attack by the nucleophiles is then directed to C(4) and C(7) and the product ratio is regulated by electronic and steric factors determined by the size of the substituents at the nitrogen atom and C(3) and also by the nature of the nucleophile:



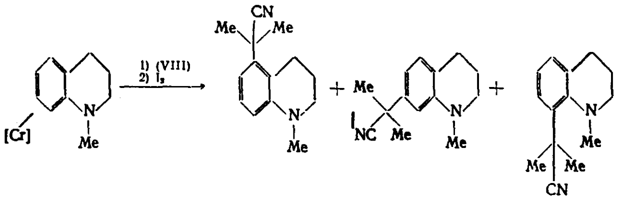
Compound (VIII) adds to the C(4) atom in the complexes with Y = H and X = NMe (XXXIII), NCH_2Ph (XXXIV), $NSiPh_2Bu$-t (XXXV), and NCO_2Bu-t (XXXVI) with a selectivity in excess of 90%. In the reaction of the complex (XXXIII), the less bulky anion $LiCH_2CN$ exhibits a lower selectivity [C(4)/C(7) = 75/25]. On the other hand, 2-lithio-1,3-dithiane and 1-lithio-3-dimethylsilylprop-2-ene reacts with the complex (XXXIII) preferentially at the C(7) atom, forming a mixture of substitution products [C(7)/C(4) = 6/1]. In contrast to the *N*-methylindole complex (XXXIII), the dithiane anion acts only on the C(4) atom in the *N*-methylindoline complex (XXXVII), which, bearing in mind the ease with which the indoline system can be converted into the indole system,


(XXXVII)


(XXXVIII)

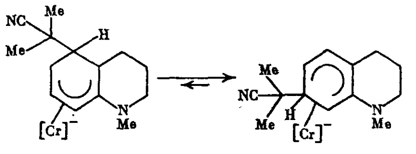
leads to the possibility of the selective synthesis of 4- and 7-substituted indoles. The addition of nucleophiles to the benzofuran complex is directed mainly to the C(4) position [C(4)/C(7) is 73/27 for R = CMe_2CN, 63/37 for R = CH_2CN, and 86/14 for R = ]. The introduction of substituents at the C(3) atom in the indole system reduces the yield of the 4-substituted product and, in the case of the complex (XXXVIII), for example, C(4)/C(7) = 17/83 for R = CMe_2CN. The opposite effect is produced by bulky substituents at the nitrogen atom [the complexes (XXXV) and (XXXVI)].

An elegant study of the reaction of (η^6-methyl-1,2,3,4-tetrahydroquinoline)ChTC with compound (VIII) revealed the influence of kinetic and thermodynamic control on the ratio of the regioisomers:[83]



(XXXIX) (XL) (XLI)

The isomer (XLI) is formed in small amounts (1–2%) and the ratio of the isomers (XXXIX) and (XL) depends on the reaction time and temperature and also on the nature of the solvent, the increase of the relative content of the isomer (XL) when the reaction is carried out in THF indicating the thermodynamic control of the reaction, while the more highly substituted anion (XLII) is converted into the sterically more favourable anion (XLIII):



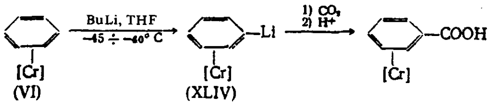
(XLII) (XLIII)

In the presence of added hexamethylphosphoramide (HMP), which strongly solvates the lithium cation, a constant ratio of the regioisomers, reflecting the kinetic control of the nucleophilic addition, is retained and in this instance there is no isomerisation. The combination of these results constitutes convincing evidence for the reversibility of the addition of nucleophiles to BCT.

IV. REACTIONS OF LITHIO-DERIVATIVES

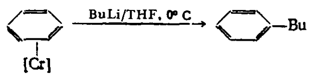
One of the most important properties of BCT is the increased acidity of the ring hydrogen atoms, which is the reason for their ability to be substituted by a metal on treatment with metallating agents. The nature of the metallating agent has a decisive influence on the direction of the process—soft nucleophiles add to the complex, while hard nucleophiles substitute a hydrogen atom.

The metallation of BCT was first achieved, by Nesmeyanov and co-workers, on treatment with BuLi; the yield of the acid after carboxylation was 19%:[84]



(VI) (XLIV)

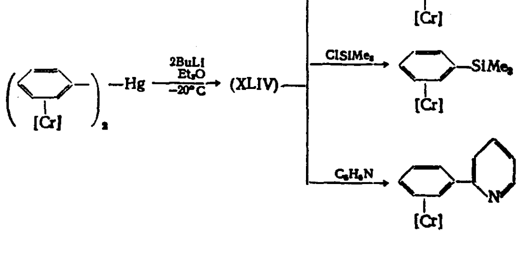
It has been shown[19,85–87] that BCT reacts with BuLi to form the complex (XLIV) almost quantitatively at −20 °C in THF but heating of the solution to 0 °C or the addition of BuLi to the BCT solution at 0 °C leads to butylbenzene in a yield greater than 80%:



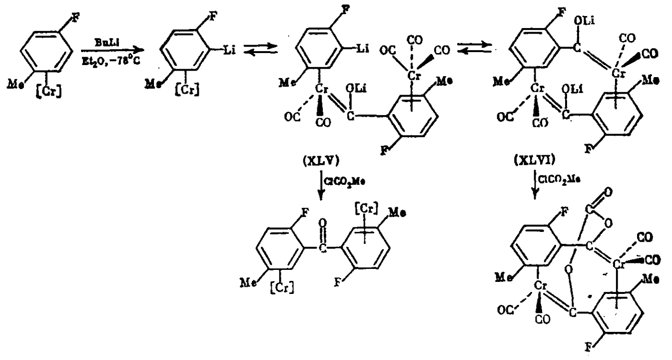
(VI)

The oxidation stage is not then required. The mechanism of the formation of butylbenzene is obscure but it is undoubtedly different from the mechanism of the coupling of soft nucleophiles to BCT.

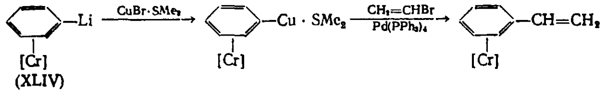
The lithio-BCT (XLIV) is readily obtained by the transmetallation reaction between dibenchrotrenylmercury and butyl-lithium and readily reacts with chlorophosphines, chlorosilanes, and pyridine:[88]



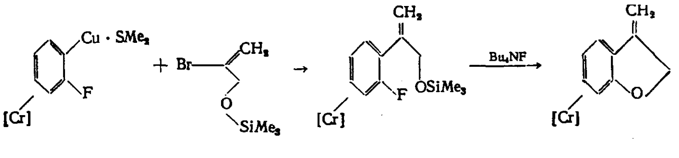
In relation to the metallation of (*p*-fluorotoluene)ChTC, it has been shown that the monomeric compounds of type (XLIV) formed at a low temperature are in equilibrium with the dimeric complexes (XLV) and (XLVI). This is manifested in reactions with electrophiles having more than one potential leaving group, for example, methyl chlorocarbonate, whereupon derivatives of benzophenone and carbonate are formed:[89]



A characteristic property of lithio-BCT is their anomalously low nucleophilicity compared with their basicity and the set of electrophiles which react with them is therefore limited.[87,90] Lithio-BCT do not react with propyl iodide and alkanesulphonates, giving rise to low yields of products even in reactions with active electrophiles such as MeCOCl and CH_2CHCH_2Br. It has been found[90] that the addition of the complex CuBr.SMe_2 to compound (XLIV) leads to copper-BCT, which react successfully with a large set of electrophiles, affording substitution products. The application of palladium catalysis made it possible to extend the scope of the reaction to include the products of cross-coupling with vinyl bromide and iodobenzene:

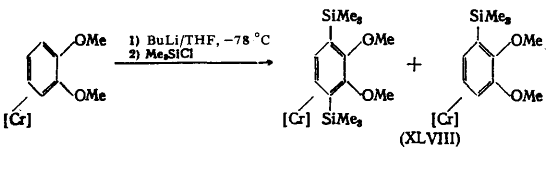


The reaction of (*o*-fluorophenyl-lithio)ChTC with the complex CuBr.SMe_2 and the subsequent coupling of the Cu-derivative with 2-bromoallyltrimethylsilyl ether give rise to the complex (XLVII), which undergoes intramolecular cyclisation, after desilylation, to the 3-methylene-2,3-dihydrobenzofuran complex:[91]



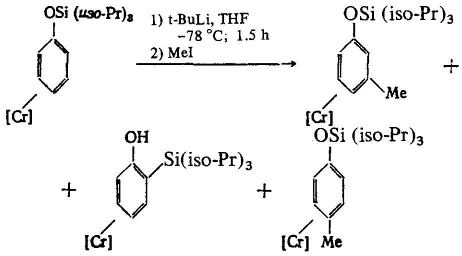
A characteristic feature of the latter is the lack of a tendency towards isomerisation to the 3-methylbenzofuran isomer, which is the product of the aromatisation of 3-methylene-2,3-dihydrobenzofuran not bound in a complex.

Metallation of (veratrole)ChTC by BuLi with subsequent silylation leads to a mixture of the mono- and di-silylated complexes in approximately equal amounts:[92]

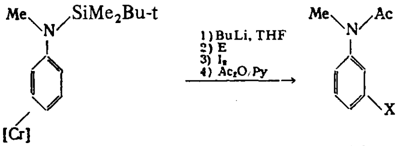


According to ^1H NMR and X-ray diffraction data, the complex (XLVIII) in solution and in the solid state has the conformation in which the bulky Me_3Si group is eclipsed by the CO group.[93]

Protection of the hydroxy-group in (phenol)ChTC leads to marked shielding of the *o*-positions and the metallation takes place in the *m*-position to the extent of 90%.[94] The yield of the *o*-substituted product does not exceed 3%:

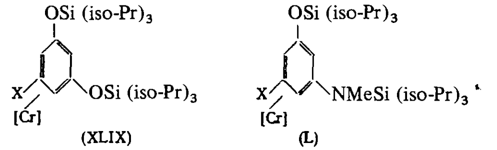


The methylation of (*N*-butyldimethylsilyl-*N*-methylaniline)-ChTC proceeds with a high regioselectivity in the *m*-position; *m*-substituted aniline can be obtained by subsequent reactions of the electrophile and the removal of ChTC.[95] The complete absence of *o*-substitution is noteworthy:



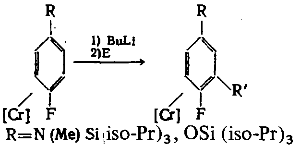
E^+=PhCHO, MeCHO, $HCONMe_2$, MeI, MeSSMe, PhCN;
X=CH (OR) Ph, CH (OH) Me, CHO, Me, SMe, COPh

The substitution of resorcinol and *m*-aminophenol by lithium takes place exclusively in the 5-position, so that the 1,3,5-trisubstituted complexes (XLIX) and (L) are formed after reactions with electrophiles:



X=Me, $SiMe_3$, CO_2Me

The metallation of tri-isopropylsilyl derivatives of *p*-fluorophenol and *p*-fluoroaniline, where the hydrogen atoms in the *o*-position relative to the fluorine atom are substituted, is especially noteworthy:

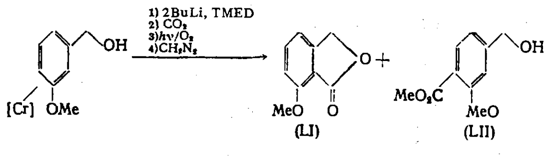


R=N (Me) Si (iso-Pr)$_3$, OSi (iso-Pr)$_3$;
R'=Me, $SiMe_3$, CO_2Me

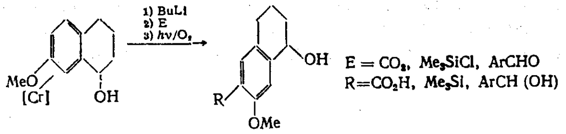
These results are the opposite to those of the metallation of sterically unhindered arenes and arenes not bound in a complex, for example, *p*-fluoroanisole and *p*-fluorodimethylaniline, where the metal always enters the *o*-position relative to the heteroatom.

The change in the regioselectivity of the metallation of the benzene ring after coordination to ChTC can be traced distinctly in relation to benzyl alcohols.[96,97] (3-Hydroxymethyl-1-methoxybenzene)ChTC reacts with two equivalents of BuLi to form the benzofuranone (LI) and the benzoic acid ester

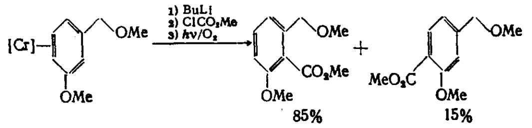
(LII) in proportions of 23 : 77 after carboxylation and methylation, while the analogous sequence of reactions with the arene not bound in a complex yields the ratio 9 : 1. With increase of the bulk of the metallating agent, the content of the 5-methylated product (LII) increases (85% for s-BuLi and 95% for t-BuLi):



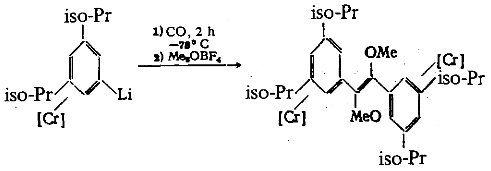
The coordination of a hard system, such as, for example, 7-methoxy-1-tetralinol, to ChTC leads to metallation exclusively in the 6-position, while the substitution of free tetralinol by lithium yields the 8-substituted product:



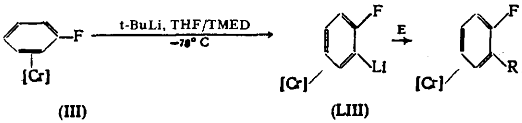
Alkyl benzyl ethers and the acetals of benzaldehydes are not *o*-metallated owing to the tendency towards deprotonation in the benzyl position with subsequent Wittig rearrangement or cleavage of the acetal linkage. The formation of a complex with TC makes it possible to metallate successfully the aromatic ring containing the above substituents with the predominant formation of 1,2,3-trisubstituted-products:



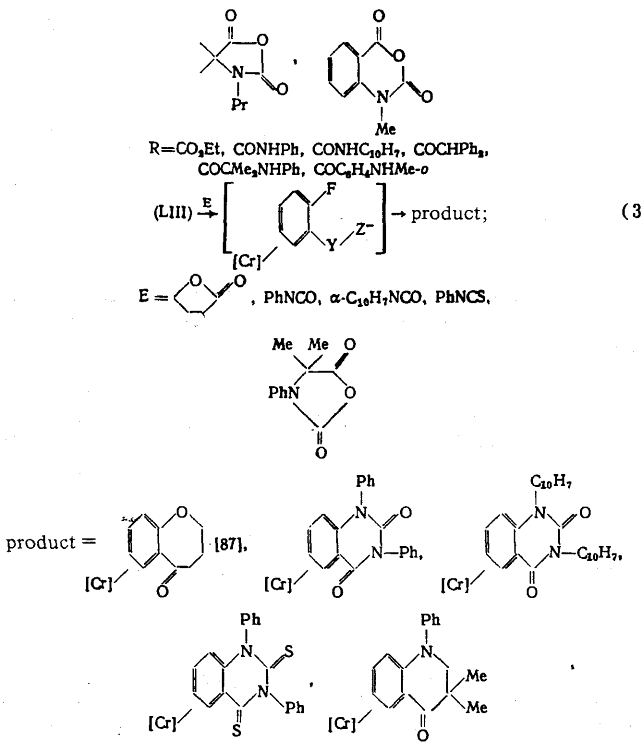
The reaction of *m*-di-isopropylbenchrotrenyl-lithium with CO and subsequent methylation with trimethyloxonium tetrafluoroborate lead to a dinuclear complex in 15% yield:[98]



A novel application of the characteristic features of benchrotrenyl systems in synthesis has been achieved by Chavshow and Widdowson,[99] who showed that the metallation of the complex (III) results in the formation of (*o*-fluorolithiobenzene)ChTC (LIII), which react smoothly with various electrophiles; depending on the ratio of the substrate and the reactant, substitution products [Eqn.(2)] or cyclisation products [resulting from the simultaneous nucleophilic substitution of the fluorine atom—Eqn.(3)] are obtained:



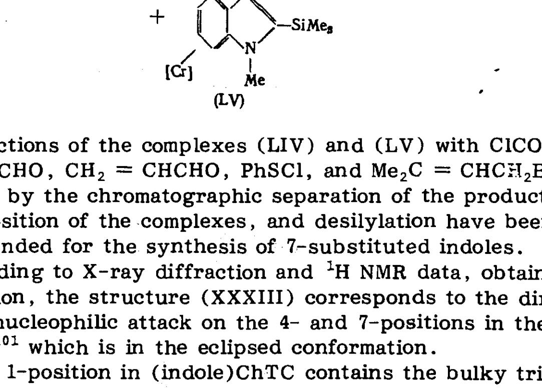
(2)



(3)

The method proposed for the synthesis of benzo-condensed systems may find an application in the chemistry of heterocyclic compounds.

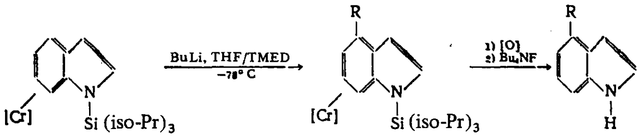
The metallation of (1-methylindole)ChTC (XXXIII) occurs in the first place in the 2-position. If this position is occupied, then attack is directed to the aromatic ring in the 7- and 4-positions in the proportions ≥4 : 1:[100]



The reactions of the complexes (LIV) and (LV) with ClCO$_2$Et, MeI, PhCHO, CH$_2$ = CHCHO, PhSCl, and Me$_2$C = CHCH$_2$Br followed by the chromatographic separation of the products, decomposition of the complexes, and desilylation have been recommended for the synthesis of 7-substituted indoles.

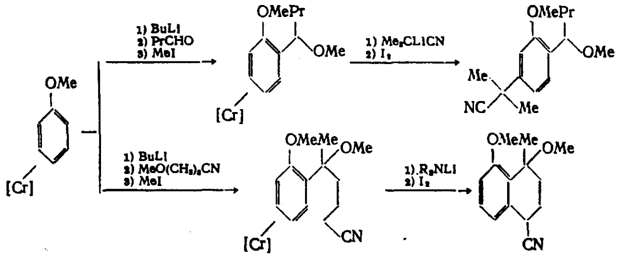
According to X-ray diffraction and ^{1}H NMR data, obtained in solution, the structure (XXXIII) corresponds to the direction of nucleophilic attack on the 4- and 7-positions in the ligand,[101] which is in the eclipsed conformation.

If the 1-position in (indole)ChTC contains the bulky triisopropyl group, then the metallation of the complex is directed mainly to the 4-position together with formation of a certain amount of 5- and 6-isomers.[102] Decomposition of the complexes and desilylation lead to 4-substituted indoles in 70% yield:



R = Me_3Si, EtO_2C, MeO_2C, PhS, $Me_2C{=}CHCH_2$

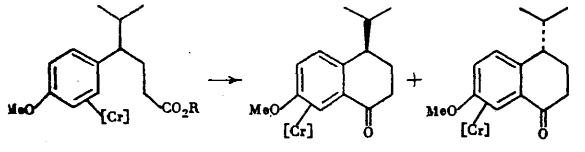
The metallation of BCT combined with nucleophilic addition or substitution has been used to synthesise trisubstituted benzenes:[87]



Favourable prospects for the employment of (lithioarene)-ChTC in synthesis, especially for the preparation of natural products, have become apparent. The synthesis of natural anthraquinones, namely 3-deoxyrabelomycin (LVI) and aclavinone (LVII),[103] is illustrated in Eqns.(4) and (5):[103]

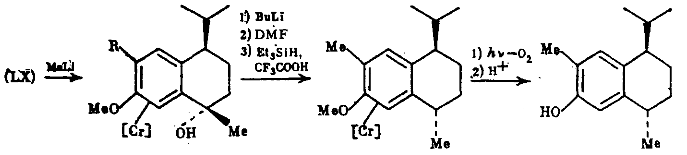
The metallation of the (tetralinol)ChTC complexes proceeds regioselectively, yielding the 6-lithio-derivatives (LVIII) and (LIX).

Temporary coordination to ChTC has been used in the synthesis of *cis*- and *trans*-7-hydroxycalamenenes.[104] The complex of 4-(*p*-methoxyphenyl)-5-methylhexanoate and $Cr(CO)_6$ was hydrolysed to the acid and the *exo*-isopropyltetralinone complex (LX) together with a small amount of the *endo*-isomer (LXI) were obtained by cyclising the acid chloride with $AlCl_3$:

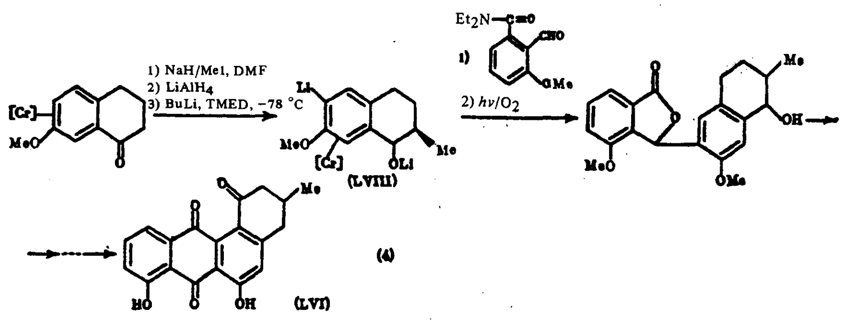


(LX) (LXI)

The reaction of the complex (LX) with MeLi leads to the *exo*-methylated product, which was metallated with BuLi in DMF and a benzaldehyde derivative was obtained. In the course of ionic hydrogenation, the reduction of the aldehyde functional group to the methyl group and hydride substitution in the benzyl position were observed simultaneously:

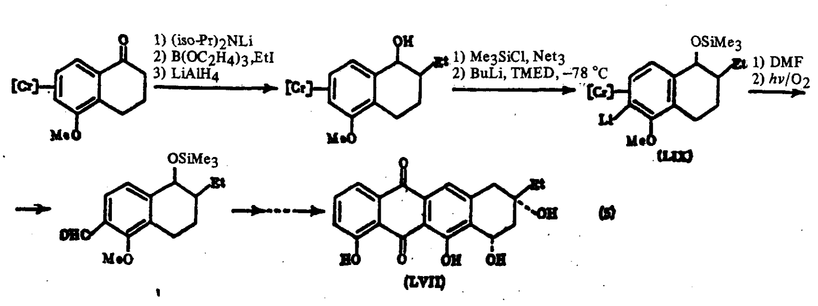


(LXII)



(LVIII)

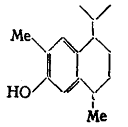
(LVI) (4)



(LIX)

(LVII) (5)

Decomposition of the complex and *O*-demethylation lead to *trans*-7-hydroxycalamenene (LXII) in a satisfactory yield. *cis*-7-Hydroxycalamenene (LXIII) was obtained from the *endo*-complex (LXI) in accordance with an analogous scheme:

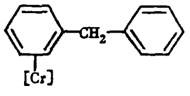


(LXIII)

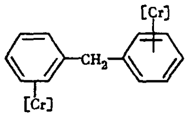
V. BENZYL ACTIVATION OF ALKYL-SUBSTITUTED DERIVATIVES

The reduced electron density on the arene ligand in BCT is responsible for the considerable increase of the acidity of the benzyl hydrogen atoms. According to an approximate estimate, their acidity in BCT derivatives is greater by two orders of magnitude than the acidity of the corresponding hydrogen atoms in the substrate not bound in the complex.[105,106]

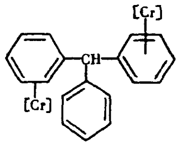
The acidifying effect of ChTC was estimated by measuring the rate of abstraction of a proton by the methoxide ion from the complexes (LXIV)–(LXVI) in the $MeOH–Me_2SO$ system:



(LXIV)



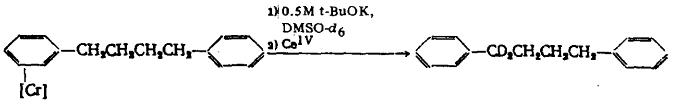
(LXV)



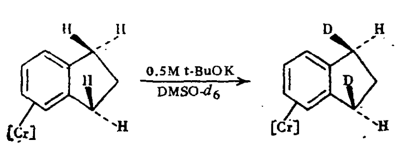
(LXVI)

Actually their kinetic acidities are similar, which has been explained by the unfavourable steric influence of the second ChTC group in diphenylmethane on the rate of ionisation of the exocyclic CH bond. However, their thermodynamic acidities increase in proportions of 1 : 2.6 : 7.4, which reflects the greater stability of the carbanion formed following the introduction of electron-accepting groups.[107]

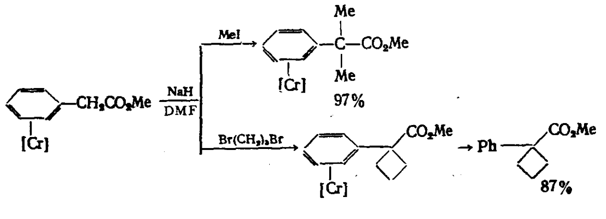
The α-hydrogen atoms of alkyl-BCT are involved in fairly rapid protophilic deuterium exchange; for example, (η^6-1,4-diphenylbutane)ChTC can be involved in the exchange with 0.5 M t-BuOK in DMSO-d_6 and after the decomposition of the complex affords 1,1-dideuterio-1,4-diphenylbutane:[108]



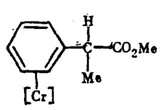
It is striking that (indan)ChTC exchanges only two of the benzyl protons, which constitutes convincing proof of the *exo*-attack by the base on the complex:



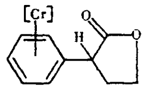
The effect of the formation of a complex with ChTC is strikingly manifested in the alkylation of phenylacetic acid esters and acetophenones.[20,109] Whereas methyl phenylacetate is not alkylated by MeI/NaH in DMF, its ChTC complex forms the dialkylated derivative almost quantitatively under these conditions and the reaction with 1,3-dibromopropene affords cyclobutane:



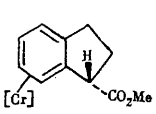
The complexes of the esters (LXVII)–(LXIX) are alkylated smoothly by the active alkyl halides RX (MeI, $PhCH_2Br$, $CH_2=CHCH_2Br$, and $HC\equiv CCH_2Br$) not only in the NaH/DMF system but also under the conditions of phase-transfer catalysis using cetyltrimethylammonium iodide:[110–112]



(LXVII)



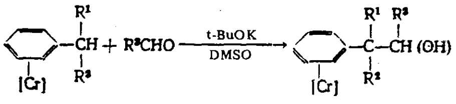
(LXVIII)



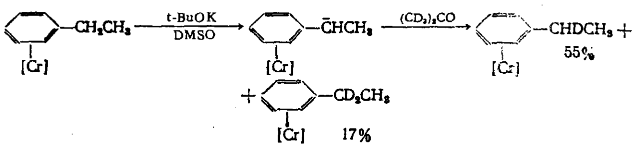
(LXIX)

The stereochemistry of the reactions is virtually the same, the electrophile attacking from the side opposite to that of ChTC.

The reaction of alkyl-BCT with formaldehyde and benzaldehyde in the presence of t-BuOK in DMSO has been used to obtain β-hydroxy-compounds, but in many instances the preparative value of the method is low owing to the low yield of products:[113,114]

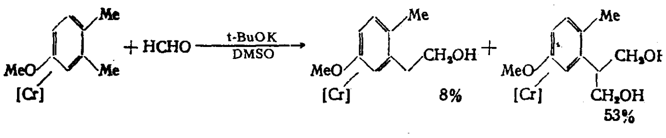


If the carbonyl compound is capable of giving rise to the enolic form, the arene complex enters only into the proton exchange reaction with formation of the corresponding alcohol:



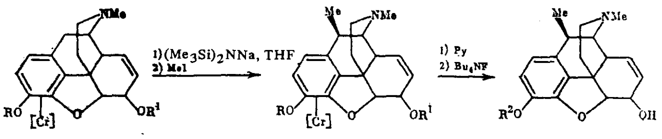
The attack by the acyclic carbanion is stereospecific and gives rise to the *exo*-product only.

It has been shown[115] that, in the presence of an alkoxy-group in the benzene ring, there is a possibility of the selective formation of α-carbanions in the *m*-position, while *p*-alkyl groups are inert:



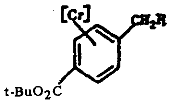
These features are responsible for the successful regio- ar stereo-specific addition of formaldehyde and alkyl halides to alicyclic compounds, especially oestrogens.[115,116]

The interaction of [6-O-t-butyl(dimethyl)silylcodeine]ChT and {3,6-bis[t-butyl(dimethyl)silyl]morphine}ChTC with $(Me_3Si)_2NNa$ and MeI leads to 10(*S*)-methyl derivatives. On subsequent decomposition of the complex with pyridine and desilylation, 10(*S*)-methylcodeine and 10(*S*)-methylmorphine are formed smoothly respectively:[117]

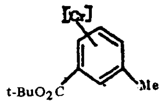


$R = R^2 = \mathrm{Me}$, $R^1 = \mathrm{t\text{-}BuMe_2Si}$; $R = R^1 = \mathrm{t\text{-}BuMe_2Si}$, $R^2 = \mathrm{H}$.

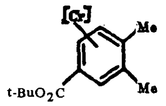
The presence of a strong electron-accepting group in the aromatic rings of the complexes alters the regioselectivity of the attack by the aldehyde in the presence of t-BuOK and activates the alkyl groups. For example, the diol, triol, and alkenol complexes (LXXIII)–(LXXVI) are formed from the complexes (LXX)–(LXXII) on reaction with formaldehyde:[118]



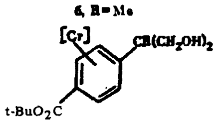
(LXX)
a, R = H
б, R = Me



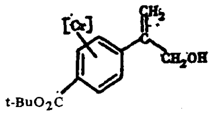
(LXXI)



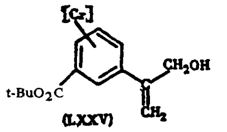
(LXXII)



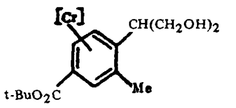
(LXXIII)
a) R = CH2OH
b) R = Me



(LXXIV)

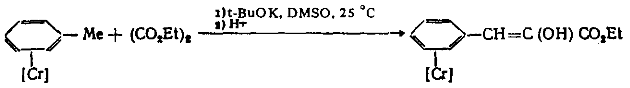


(LXXV)

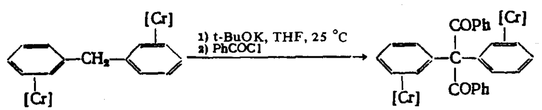


(LXXVI)

The reaction of (toluene)ChTC with t-BuOK in the presence of diethyl oxalate leads to a stable enol, derived from phenylpyruvic acid, whose structure has been demonstrated by X-ray diffraction:[119,120]



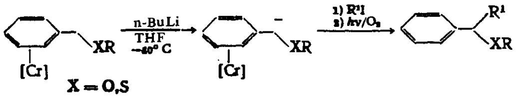
The α-protons in alkyl-BCT are readily abstracted in the reaction with t-BuOK in THF and the carbanions formed react with MeI,[121,122] diethyl oxalate and benzaldehyde,[123] and PhCOCl,[121] for example:



(LXV) 56%

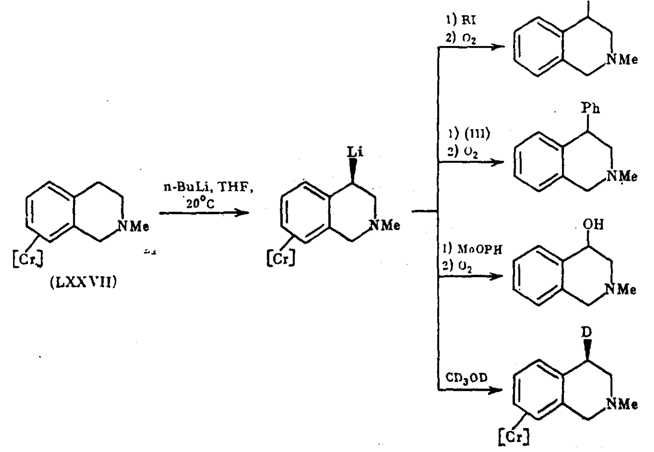
The α-metallation of alkyl-BCT by the KH/18-crown-6 ether system has been described.[124]

The α-metallation of certain BCT derivatives is achieved effectively with the aid of butyl-lithium and in this respect the ChTC derivatives of alkyl benzyl ethers and alkyl benzyl sulphides exhibit interesting features.[125] The α-carbanions derived from alkyl benzyl ethers and sulphides readily undergo the Wittig rearrangement, while coordination with ChTC leads to the possibility of achieving smoothly alkylation by various agents with formation, after the decomposition of the complex, of α-substituted benzyl ethers:



X = O,S

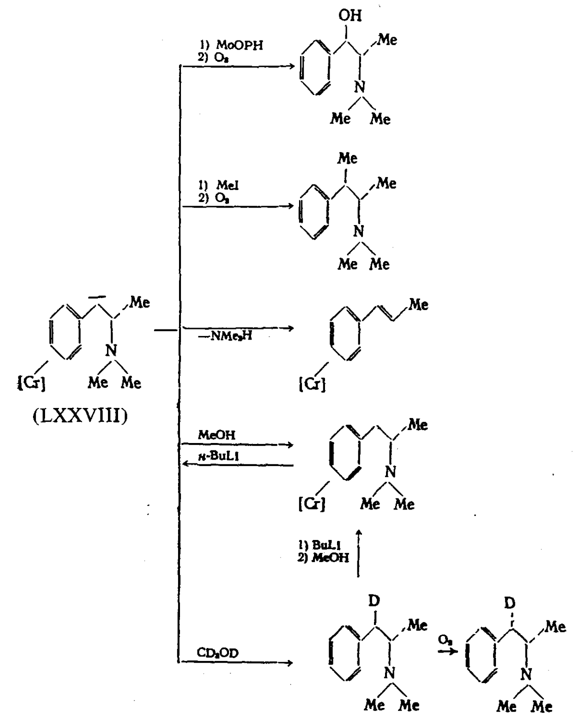
The formation of the transient complex between the aromatic ring and ChTC proved to be useful in the selective synthesis of 4-substituted 1,2,3,4-tetrahydroisoquinolines, which exhibit a selective pharmacological activity.[126] Metallation of the complex (LXXVII) leads to the substitution of the *exo*-hydrogen in the 4-position and the formation of a lithio-derivative, which is alkylated smoothly by alkyl halides, is phenylated by (fluorobenzene)ChTC, and reacts with oxodiperoxomolybdenumhexamethylphosphoramide (MoOPH) to form a 4-*exo*-hydroxylated product:



(LXXVII)

The coordination of *NN*-dimethylamphetamine to ChTC stabilises the corresponding benzyl carbanion in relation to the elimination of the amino-group and makes it possible to carry out smoothly stereospecific benzyl substitution.[127]

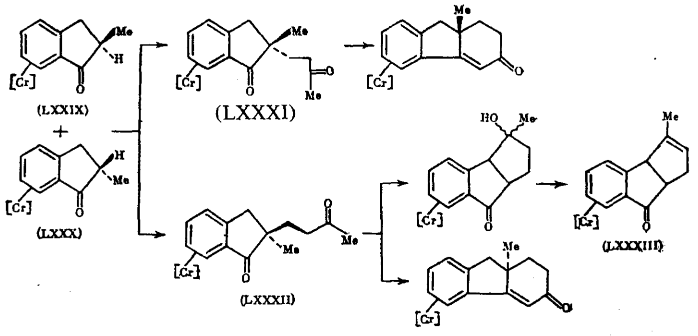
Metallation of the complex (LXXVIII) by n-BuLi at −40 °C and above leads to the elimination of Me_2NH and the formation of (*E*-β-methylstyrene)ChTC. However, at −78 °C the anion formed initially is stable and readily reacts with electrophiles (MeI, MoOPH, CD_3OD) to form derivatives of the complex (LXXVIII), from which free radicals are readily produced:



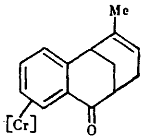
(LXXVIII)

A notable feature of the above substitution reactions is their high stereospecificity.

The increased acidity of the α-hydrogen atoms in BCT constitutes the basis of the synthesis of certain condensed systems, modelling natural products, from indanone and tetralinone complexes.[128,129] Thus the diastereoisomers (LXXIX) and (LXXX), which exist in equilibrium in acid and basic media, readily undergo the Michael reaction with methyl vinyl ketone in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene to form two adducts—the *exo*-adduct (LXXXI) and the *endo*-adduct (LXXXII) in proportions of 13 : 87. The complexes are able to undergo a base-catalysed cyclisation and compound (LXXXII) affords mainly (>90%) the products of cyclisation at the benzyl position, the unsaturated tricyclic system (LXXXIII) being obtained after dehydration:



The system (LXXXIV) has been obtained analogously from tetralinone complexes:

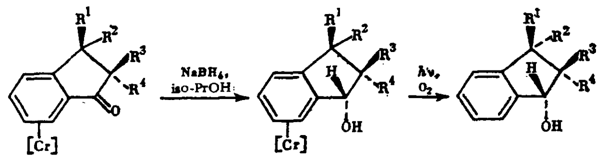

(LXXXIV)

The, at first sight, anomalous *exo*-attack by the ketone on the benzyl position becomes readily explicable from the standpoint of the activating effect of ChTC on the hydrogen atom in the α-position. In view of the regioselective activation of the benzyl CH bond, the stereochemical control of the annelation reaction, and the ease of the regeneration of the arene ligand from its TC complex, the method is exceptionally useful for the synthesis of various optically active compounds.

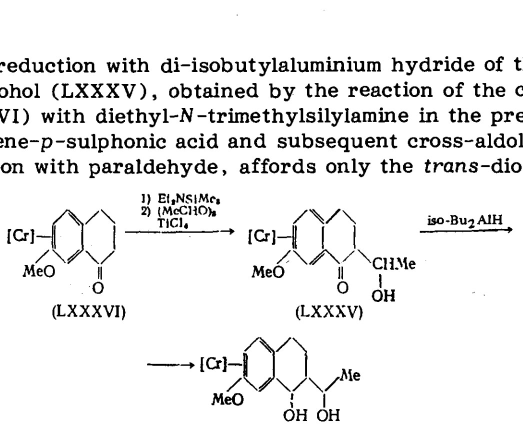
VI. STEREOCHEMICAL FEATURES OF ARENECHROMIUM TRICARBONYLS

The coordination of an arene to ChTC leads to the steric shielding of one of the sides of the aromatic ligand, which is the reason for the *exo*-attack by various agents on this ligand and for the direct binding of the functional groups with it.

The hydride reduction of (indanone)ChTC, (tetralinone)ChTC,[130] and various (alkylindanone)ChTC (*exo* and *endo*-, α- and β-) [131–134] proceeds stereoselectively and leads to the formation of *endo*-alcohols. The amount of *exo*-alcohols did not exceed 10% in any one instance, amounting to 3% as a rule. Together with the quantitative decomposition of the complexes, this property provides an effective pathway to *cis*- and *trans*-indanols, for example:

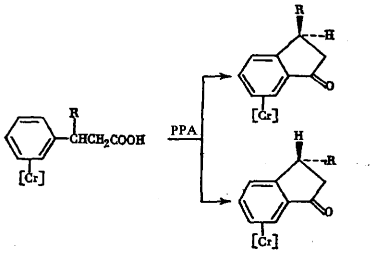


The reduction with di-isobutylaluminium hydride of the ketoalcohol (LXXXV), obtained by the reaction of the complex (LXXXVI) with diethyl-*N*-trimethylsilylamine in the presence of toluene-*p*-sulphonic acid and subsequent cross-aldol condensation with paraldehyde, affords only the *trans*-diol:[135]

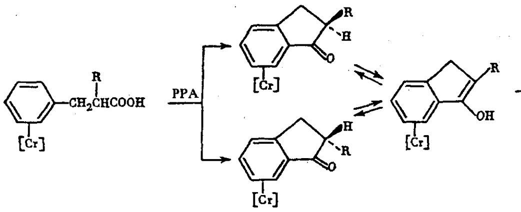


In the absence of the ChTC group, a mixture of the *trans*- and *cis*-diols is formed in proportions of 12 : 88.

When the α- and β-alkyl-substituted benchrotrenylpropionic acids are cyclised, a definite regular behaviour is observed—the amount of *exo*-isomer increases with increase of the bulk of the substituent. The 2-indanone complexes formed can undergo the *exo* ⇌ *endo* transitions via the intermediate enolic form:[131,132]



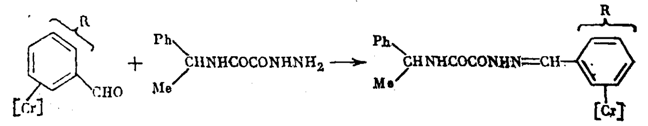
R	*exo/endo*
Me	65/35
Et	80/20
iso-Pr	95/5



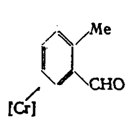
R	*exo/endo*
Me	48/52
Et	60/40
iso-Pr	75/25
t-Bu	95/5

PPA = polyphosphoric acid.

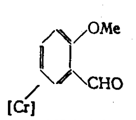
Chiral BCT with functional-group substituents, characterised by both planar and central chirality, are of special interest for asymmetric synthesis. BCT with two different substituents in the *o*- or *m*-positions are chiral and can be resolved into optical isomers.[136–143] For example, the resolution of the racemates of aldehydes has been achieved with a high yield via their reaction with (*S*)-(−)-5-(α-phenylethyl)-semioxamazide with subsequent chromatography. Acid hydrolysis results in the quantitative regeneration of the optically pure aldehydes:[144]



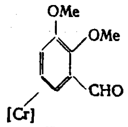
The aldehydes (LXXXVI)–(XC) have been resolved into the optically pure isomers by this method:



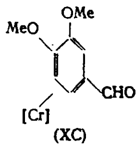
(LXXXVII)



(LXXXVIII)

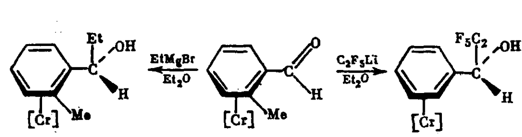


[LXXXIX]



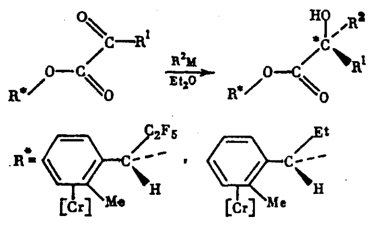
(XC)

The reaction of the optically active aldehyde (LXXXVII) with ethylmagnesium bromide or perfluoroethyl-lithium gives rise to alcohols with an enantiomeric excess of 100 and 88% respectively:[145]



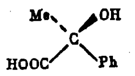
E.E. 100% (+)15-(LXXXVII) E.E. 88%

The chiral alcohols obtained were used in the Prelog type synthesis:

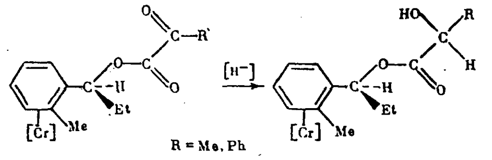


R^1 = Me, Ph; R^2 = C_2F_5, Me, PrC≡C, Ph

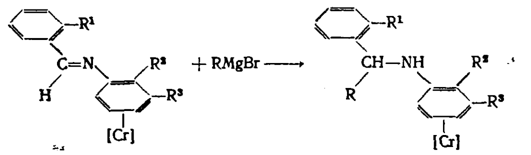
The asymmetric synthesis proceeds with a high enantiomeric excess (between 85 and 100%); for example, (+)-*S*-atrolactonic acid has been obtained by the addition of MeMgI to the optically pure ketoester and subsequent hydrolysis:



The reduction of a chiral α-ketoester by various reductants to α-hydroxyesters has been investigated:[146]



A high percentage of asymmetric induction is observed when "L-selectide" LiBH(Bu-s)$_3$ is used as the reductant (E.E. = 84–90%). Just as high a degree of asymmetric induction has been obtained in reactions of Grignard reagents with complexes of aromatic Schiff bases (XCI):[147]

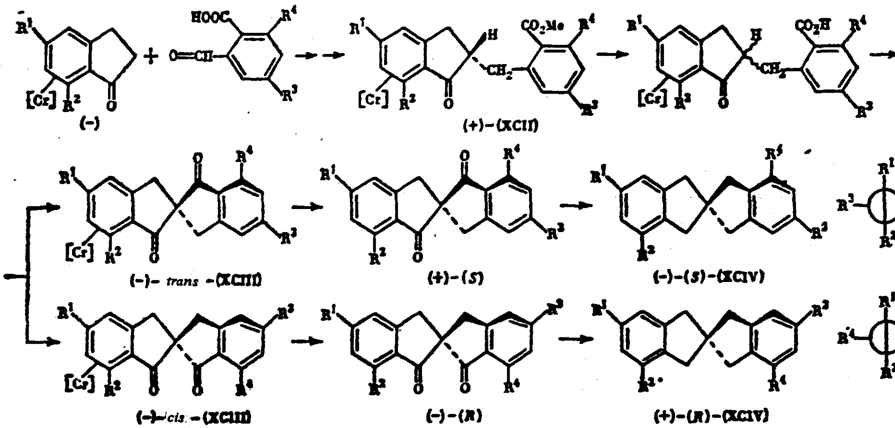


R = Me, PhCH$_2$;
R^1 = H, Me, OMe, Cl;
R^2 = H, Me, Et, Ph;
R^3 = H, Me

When an asymmetric Grignard reagent was allowed to react with (benzophenone)ChTC and (fluorenone)ChTC, partly resolved tertiary alcohols were obtained.[148]

The formation of complexes with ChTC had led to a simple and universal method of the synthesis of optically active benzospirans with a specific chirality from optically active (1-indanone)ChTC.[149,150]

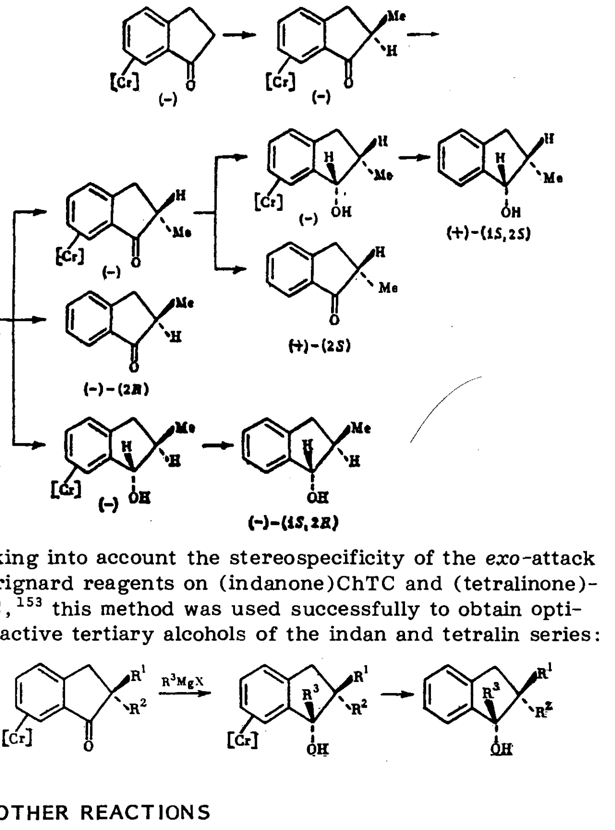
The condensation of the complex with phthalic monoaldehyde [*o*-formylbenzoic acid?] produced a benzylidene complex from which the *endo*-benzyl derivative (XCII) was obtained after esterification and hydrogenation. On alkaline hydrolysis of the latter, epimerisation at the C(2) atom of the indanone was observed. Cyclisation of the complexes with polyphosphoric acid leads to a readily resolvable mixture of diastereoisomeric spiroindanone complexes—the *cis*- and *trans*-isomers of compound (XCIII). Optically active 2,2′-spirobi-indans (XCIV) were obtained by the decomposition of the complexes to 2,2′-spirobi-indan-1,1′-diones and subsequent catalytic hydrogenation:



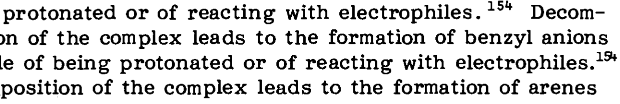
R^1, R^2, R^3, R^4 = H, Me, OMe

A cycle of reactions with the optically active complexes (I) and (II) has been carried out by Jaouen and Meyer.[151,152] The racemic compounds (I) and (II) were resolved into their enantiomers by the fractional crystallisation of the cinchonidinium salts of their acid succinates. Optically active indanone and tetralinone complexes are obtained by oxidising the corresponding alcohols with MnO_2 and the decomposition of the complexes of the enantiomers leads to optically active alcohols.

The *exo*-alkylation of the complexes in the 2-position leads to the formation of a new asymmetric centre in the system and creates a convenient preparative method of synthesis of optically active 2-methylindanones, 2-methyltetralinones, and the *trans*-alcohols. The possibility of obtaining the *cis*-alcohols from 2-methyl-*endo*-ketone complexes has been demonstrated in principle, although the separation of the *exo*- and *endo*-isomers requires a special technique. The reactions involved (indanone)ChTC, but all the characteristics are valid also for (tetralinone)ChTC:[151,152]

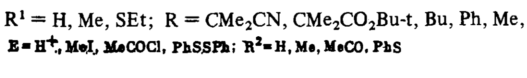


Taking into account the stereospecificity of the *exo*-attack by Grignard reagents on (indanone)ChTC and (tetralinone)-ChTC,[153] this method was used successfully to obtain optically active tertiary alcohols of the indan and tetralin series:

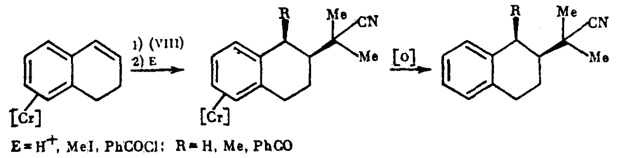


VII. OTHER REACTIONS

The reaction of vinyl-BCT with carbanions opens up wide prospects for organic synthesis.[154] It has been shown that a fairly large set of nucleophiles add to the β-position of the η^6-styrene ligand with formation of benzyl anions capable of being protonated or of reacting with electrophiles.[154] Decomposition of the complex leads to the formation of benzyl anions capable of being protonated or of reacting with electrophiles.[154] Decomposition of the complex leads to the formation of arenes with functional-group substituents:

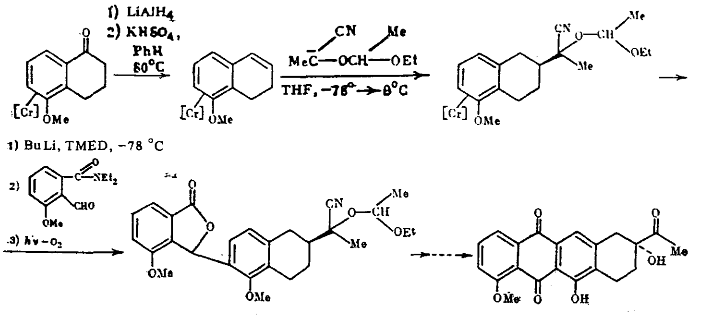


R^1 = H, Me, SEt; R = CMe_2CN, CMe_2CO_2Bu-t, Bu, Ph, Me, etc;
E = H^+, MeI, MeCOCl, PhSSPh; R^2 = H, Me, MeCO, PhS



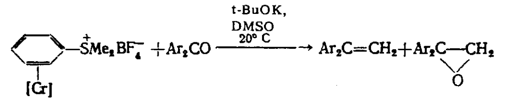
E = H^+, MeI, PhCOCl; R = H, Me, PhCO

The application of BCT to the synthesis of 11-deoxyanthracyclinones, exhibiting an anti-cancer activity, has been described.[155] The method is based on the characteristic features of the addition of the carbanion to alkenyl-BCT and on the regioselectivity of the metallation of the coordinated methoxyarene:



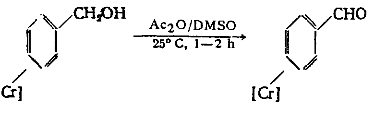
Among the practical aspects of the application of the BCT, mention should be made of their use as catalysts of the hydrogenation of dienes and polyenes[156,157] and as a label in molecular biology.[158–160]

On reaction with aldehydes and ketones, benchrotrenylsulphonium ylides form mixtures of an oxiran and an olefin, while purely organic sulphonium ylides produce only oxirans in this reaction:[161]

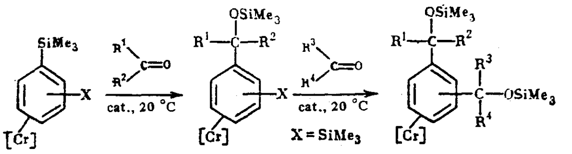


Preliminary results on the activating effect of the formation of complexes with ChTC on the oxidation of diphenylmethane to benzophenone have been published.[162] Whereas diphenylmethane is not oxidised by KO_2 in dimethyl sulphoxide, the complexes $(Ph_2CH_2)Cr(CO)_3$ and $(Ph_2CH_2)[Cr(CO)_3]_2$ are converted into benzophenone in 59 and 63% yields respectively.

A general method has been proposed for the oxidation of benchrotrenylcarbinols to aldehydes without the removal of ChTC, in 55–75% yield:[163]

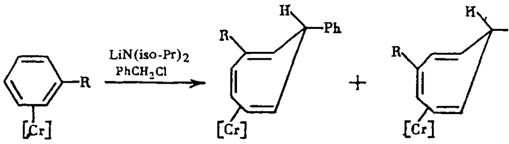


Mono- and bis-(trimethylsilyl)-BCT readily enter into reactions with aldehydes and ketones catalysed by t-BuOK or CsF, forming products of addition to the C=O groups:[164]



The electrochemical reduction of (benzophenone)ChTC, $(benzophenone)(ChTC)_2$, and (fluorenone)ChTC in the presence of 1,3-dibromopropane[165] and acetic or benzoic anhydride[166] has been recommended for the synthesis of diphenylmethyl derivatives.

The reaction involving ring expansion in the aromatic ligand in alkylbenchrotrenes on treatment with $PhCH_2Cl$ and lithium di-isopropylamide is of interest:[167]



According to X-ray diffraction data, the phenyl group has the *endo*-orientation. The reaction has been extended to Ph_2CHCl and $CH_2{=}CHCH_2Cl$.

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Physicochemical Properties of Layered Compounds of Graphite

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The results of studies carried out in recent years on certain physicochemical properties (heat capacities, enthalpies of formation, compressibilities, thermal expansions, and thermal stabilities) of layered compounds of graphite are surveyed. The bibliography includes 126 references.

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I. INTRODUCTION

Many compounds with anisotropic layered structures (typical representatives of which are graphite and transition metal dichalcogenides), in which the bonding forces between the species within the layer are much stronger than between the layers, are able to form compounds of a new type as a result of the insertion of various substances in the interlayer space. Among compounds of this kind, those of graphite occupy the principal place, which is in many respects due to the possibility of their extensive application in various fields.

Many substances (metals, alloys, metal halides, oxides, acids, etc.) capable of being inserted in the graphite lattice with formation of new compounds are now known. However, despite the fact that the synthesis of such compounds was described as early as the first half of the past century, their systematic investigation began only about 40 years ago and such research has developed on a wide scale only in the last 25 years.

We may note that hitherto there has been no single terminology in the naming of compounds of this kind. Thus in the Soviet literature they are usually referred to as layered compounds of graphite, graphite interstitial compounds, graphite occlusion compounds, graphite clathrate compounds, graphite intercalation compounds, intercalated graphites, or simply graphitides. In foreign literature they are called "graphite intercalation compounds", "graphite lamellar compounds", intercalated graphites", and "graphitides", although according to the recommendations of the latest International Conference on these compounds[1] it is recommended that the term "graphite intercalation compounds" (abbreviated to GICs) be used.

We shall henceforth employ mainly the term "graphite layered compounds" (GLC), because in our view it emphasises the layered character of the structure of these compounds. The term "graphite interstitial compound" (GISC) appears to be less apt, since the term "interstitial phases" is usually employed, for example in the metallurgical literature, for the designation of completely different substances. The term "graphitides" can be applied only to compounds of graphite with metals or alloys, because it emphasises the difference between compounds of this class and the carbides and acetylides of the corresponding metals.

As mentioned above, the growing interest in GLC is in many respects due to the constantly expanding fields of their practical application. Thus GLC catalyse various processes (for example, the synthesis of ammonia, artificial diamonds, etc.[2,3]); they are good conductors of electricity and can be used as cathodic materials in chemical current generators.[4] The use of GLC in systems designed for the storage of "thermal" energy,[5] as additives for the improvement of the physicomechanical properties of certain types of abrasive materials and powdered alloyed steels, and also as the raw material for the preparation of a new variety of carbon materials with regulated physicochemical properties, the so-called thermally cleaved graphite,[6] is promising. The increasing interest in GLC is indicated by the establishment in the USA of the Intercal Company specialising in the practical application of these compounds.

In order to be able to predict the behaviour of GLC under operating conditions and for the optimisation of their preparation processes, it is essential to have information about their physicochemical properties. Such information also makes it possible to understand the nature and characteristic features of the interspecies interaction in GLC, which is of considerable practical interest. However, hitherto there have been comparatively few data in the literature on the thermodynamic properties, compressibilities, thermal expansion, and thermal stability of GLC;[7-27] some of the individual properties of the GLC listed above have been subjected to a critical examination in early review publications.[28-35]

In recent years there has been a sharp growth of studies of the properties of GLC (see, for example, Refs.36–42). Regular international conferences on GLC are being held and the international scientific journal "Synthetic Metals", specialising to a large extent in the publication of data on GLC, has been organised. Numerous papers presenting the results of studies on certain physicochemical properties of GLC have been published.

The aim of the present review is to give a systematic critical account and a survey of the literature data of recent years obtained in studies of the heat capacities enthalpies of formation, the influence of high pressure on the properties, thermal expansion, and thermal stabilities of GLC.

II. THERMODYNAMIC PROPERTIES

Hitherto there have been few systematic studies designed to determine experimentally the thermodynamic properties of GLC† (see, for example, Refs.7–13), although in recent years several attempts have been made to carry out such investigations by a calorimetric method.

The heat capacity *Cp* of the lithium graphitide C_6Li has been investigated[43] in the range 4–300 K and a small anomaly was observed in the heat capacity at ~200 K which, according to the authors,[43] can be related to a structural phase transformation of the compound. The heat capacities of GLC with bromine, containing 0.5, 2.2, and 9.6 at.% of bromine, have been measured in the temperature range 1.5–6 K and the electronic component of the heat capacity as well as the Debye temperatures were calculated.[44] It was shown that the bromine atoms are insignificantly ionised (~1%) in all the GLC.

With the aid of differential scanning calorimetry (DSC), Wu and Vogel[45] investigated stage 1 GLC with antimony pentafluoride in the range 4.2–300 K; a phase transformation of the "order–disorder" type was observed near 185 K. Unfortunately the above authors[45] do not quote either the composition of the GLC investigated or any numerical values of its thermodynamic functions. The heat capacities *Cp* and magnetic susceptibilities of the GLC $C_{6.2}FeCl_3$, $C_{17}FeCl_3$, and $C_{11.3}NiCl_2$ have been measured.[46] An anomalous behaviour of the heat capacities of the compounds was observed in the vicinity of 4, 1.7, and 20 K respectively and the authors[46] attributed them to the occurrence in the compounds investigated of transitions to states of the "spin glass" type. In the study of stage 2 GLC with $NiCl_2$, Suzuki et al.[47] observed two regions of anomalous behaviour of the magnetic susceptibility at 18.0 and 21.3 K. However, heat capacity measurements revealed an anomaly only in the vicinity of the second temperature but no appreciable changes in heat capacity were observed at the first temperature. Murakami et al.[51] investigated stage 2 GLC with $CoCl_2$ and observed two magnetic transitions at 8.0 and 9.1 K. The temperature variation of the heat capacity of this compound revealed an anomaly only at the second temperature.

A low-temperature DSC study of GLC with titanium(IV)[48] and tin(IV)[49] chlorides showed that the decomposition of the compound with $TiCl_4$ is observed at 247 ± 1 K (the melting point of $TiCl_4$ is $T_m = 249$ K[48]) and that of the compound with $SnCl_4$ occurs at 237 ± 1 K ($T_m = 240$ K for $SnCl_4$ [49]) regardless of the stage of the compound, i.e. the GLC decompose at temperatures close to the melting points of the intercalants. A DSC study of the products of the reduction of GLC with $SnCl_4$ by potassium showed[50] that the enthalpy of decomposition of the compounds (with fusion of the intercalated tin) is close to the enthalpy of fusion of pure tin, which indicates a weak interaction of the latter with the graphite lattice. Unfortunately none of the past studies[48-50] quote numerical values of *Cp* for the GLC.

A DSC investigation of the *Cp* of the unsaturated stage 1 GLC $C_{32}SbCl_{4.7}$ [52] revealed a phase transition to the vitreous state at 210 K; on the other hand, the transition did not occur for the saturated stage 1 compound. In a DSC study of the stage 1 GLC C_8Cs, Ubbelohde and Drummond[53] observed a phase transformation at ~250 K whose form depended to a large extent on the type of graphite used for the synthesis. They also estimated the enthalpy and entropy of the observed phase transformation, amounting to ~111.7 J g-atom^{-1} and 0.4 J g-atom^{-1} K^{-1} respectively.

Suematsu et al.[54] investigated the heat capacity of the graphitide $C_{24}Rb$ below room temperature and observed four anomalies in the heat capacity at 48, 103, 162, and 210–220 K, which are associated with phase (including structural) transformations. However, no numerical values of the corresponding thermodynamic functions are quoted in the above study.[54] The heat capacity of the stage 1 compound $C_{10}Al.Cl_{3.3}$ has been investigated by DSC in the range 120–300 K[55] and an anomaly has been found in *Cp* near 226 K, associated with a transformation of the "order–disorder" type, whose enthalpy was 900 ± 50 J mol^{-1}, which is within the same limits as for other GLC; the entropy of this transformation has been estimated as 4.0 ± 0.5 J mol^{-1} K^{-1} (Fig.1). However,

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†Depending on how many carbon layers separate two nearest layers of the intercalant, GLC are subdivided into compounds with stage 1, stage 2, etc. intercalation.[1] Depending on the degree of filling of the intercalant, GLC are subdivided into saturated (with the limiting content of the adduct) and unsaturated (for which the content of the adduct is less than the limiting value).

no anomalies have been observed in the experimental temperature range for stage 4 GLC with $AlCl_3$ of the type $C_{50}Al.$ $.Cl_{3.3}$.[55]

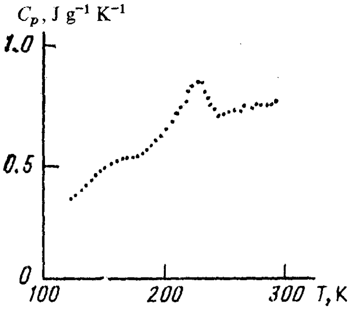

Figure 1. Temperature variation of the heat capacity of the compound $C_{10}AlCl_{3.3}$.[55]

The heat capacities of the compound C_6FeCl_3 (stage 1) and $C_{12}FeCl_3$ (stage 2) have been measured[56] by the DSC method in the range 298–570 K with an error of ±2.8%; the temperature dependence of the heat capacity (J mol^{-1} K^{-1}) of the compounds investigated is described by the equations

$$C_p(C_6FeCl_3) = 141.7 + 0.037T$$
$$C_p(C_{12}FeCl_3) = 176.0 + 0.277T.$$

We may note that, according to a number of data,[27,57–61] the decomposition of the GLC with $FeCl_3$ begins at ~573 K to which should correspond an anomalous change in Cp near 573 K. However, the authors[56] observed no anomalies in the $Cp(T)$ relation. Such discrepancy between the data of different investigations can be explained, in particular, by the different methods of synthesis of the compounds and the different composition and type of graphite used in the synthesis.

The heat capacities of GLC with certain 3*d* metal chlorides, namely $C_{4.68}CuCl_2$ (stage 1), $C_{6.35}CuCl_2$ (stage 1), $C_{7.73}CuCl_2$ (stage 1 with an admixture of stage 2),[62,63] $C_{6.97}CoCl_2$ (stage 1), $C_{16.8}CoCl_2$ (stage 2),[63] $C_{7.7}FeCl_3$ (stage 1),[58,59] $C_{11.83}FeCl_3$ (stage 2),[58] $C_{16.2}NiCl_2$ (stage 2), and $C_{5.5-6.5}\cdot$ $.MnCl_2$ (stage 1),[64] have been investigated[58,59,62–64] by the triple thermal bridge method (with an error ≤ 3%). The experimental results are presented in Figs.2 and 3. Least squares treatment of the results yielded the coefficients *a*, *b*, and *c* in the equations relating the heat capacities of the GLC investigated to temperature (Table 1). For the compounds $C_{7.7}FeCl_3$, $C_{11.83}FeCl_3$, and $C_{5.5-6.5}$-$MnCl_2$, the authors[58,59,64] observed anomalies in the heat capacity with maxima at 455 ± 5, 445 ± 5, and 450 ± 2 K respectively, associated with reversible solid-phase transformations of the GLC. The enthalpies of the above transformations were found to be 0.13 ± 0.03 kJ mol^{-1}, 2.78 ± 0.41 kJ mol^{-1}, and 1.33 J g^{-1}.

We may note that no anomalies in the heat capacities of the saturated GLC with $FeCl_3$, having the compositions C_6FeCl_3 and $C_{12}FeCl_3$, have been observed.[56] One of the causes of the discrepancy between the result of the studies of Skoropanov and co-workers[58,59] and Solozhenko et al.[56] for the GLC $C_{7.7}FeCl_3$ and C_6FeCl_3 may be the fact that, as in the case of the GLC with $SbCl_5$,[52] in the unsaturated compound, in contrast to saturated compounds, the transition within the layer involving a change in the structure of the intercalated component are sterically unhindered. Account should also be taken of the different methods of synthesis of the compounds by Skoropanov and co-workers[58,59] and Solozhenko et al.[56] and also of the differences in the type of graphite matrix.

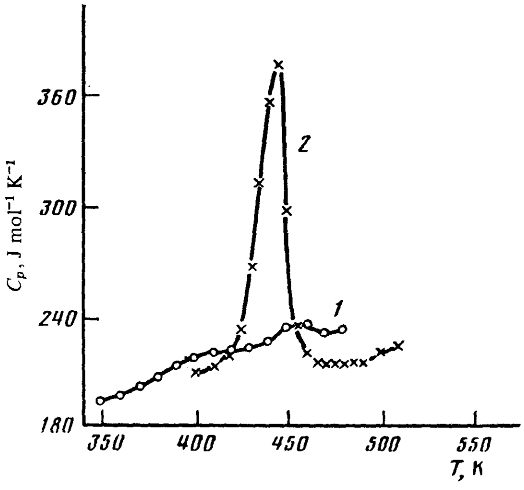

Figure 2. Temperature variation of the heat capacity of the GLC with $FeCl_3$:[58,59,62–64] 1) stage 1; 2) stage 2.

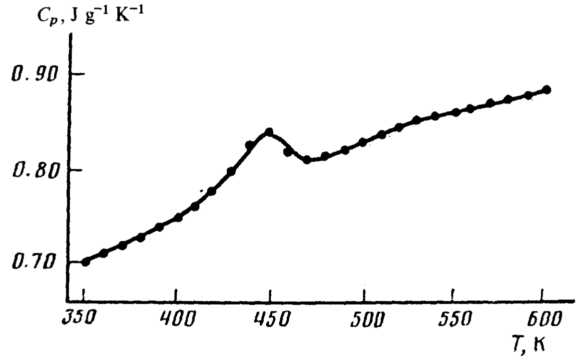

Figure 3. Temperature variation of the heat capacity of the compound $C_{5.5-6.5}MnCl_2$.[64]

The enthalpy of the reaction

$$16C_{graphite}(cryst.) + Br_2(liq) \rightleftarrows C_{16\pm0.3}Br_2(cryst.)$$

has been determined at 308.0 ± 0.5 K[65] and the enthalpy of formation of the compound $C_{16\pm0.3}Br_2$ has been calculated as −16.43 ± 0.76 kJ mol^{-1}.

On the basis of isobaric-thermoanalytical studies, Solozhenko et al.[56] calculated the standard enthalpies of formation of stage 1 and stage 2 GLC with $FeCl_3$:

$$\Delta H^0_{f,298}(C_6FeCl_3) = -(491 \pm 13)\ \text{kJ mol}^{-1};$$
$$\Delta H^0_{f,298}(C_{12}FeCl_3) = -(456 \pm 10)\ \text{kJ mol}^{-1}.$$

III. THE INFLUENCE OF HIGH PRESSURES

The study of GLC at high pressures is of considerable theoretical and practical interest, especially in connection with the possibility of employing GLC in the synthesis of artifician diamonds.[3] However, the majority of studies have been devoted to the investigation of the influence of pressure on the electronic or electrical properties of GLC and also on their structure. At the same time data on the compressibilities and phase transformations of GLC under the influence of high pressures are of significant interest.

Table 1. The coefficients *a*, *b*, and *c* in the equation for the temperature variation of the heat capacity: C_p (kJ mol^{-1} K^{-1}) = $a + 10^{-3}bT + 10^6cT^{-2}$.[58,59,62–64]

Compound	*a*	*b*	*c*	*T*, K **
$C_{4,68}CuCl_2$	104.729	95.1342	−2.01471	350—550
$C_{6,35}CuCl_2$	72.9829	121.622	1.00163	370—520
$C_{7,73}CuCl_2$	190.694	−37.0157	−5.68839	370—500
$C_{6,97}CoCl_2$	130.236	97.2574	−2.23586	350—600
$C_{16,8}CoCl_2$	244.854	209.482	−8.54369	350—600
$C_{7,7}$ FeCl$_3$	−157.539	815.818	7.94588	350—410
$C_{16,2}NiCl_2$*	0.721254	0.561208	−0.0226657	350—600
$C_{5,5+6,5}MnCl_2$*	−0.323501	2.18667	0.0315135	350—400
	0.969003	0.0680034	−0.0426992	480—600

*For $C_{16.2}NiCl_2$ and $C_{5.5-6.5}MnCl_2$, C_p was expressed in J g^{-1} K^{-1}; for $C_{5.5-6.5}MnCl_2$, the coefficients *a*, *b*, and *c* were calculated by ourselves from the data of Petrov et al.[64]
**Temperature range.

Table 2. The compressibilities of the GLC with HNO_3 and $SbCl_5$.[66,67]

Compound	Stage	$10^{-3}K_c$, kbar^{-1}	$10^{-3}K_a$, kbar^{-1}
Graphite	—	2.9±0.3	0.1±0.3
GLC with HNO_3	3	5.0±0.7	0.0±0.3
GLC with $SbCl_5$	2	2.0±0.5	0.0±0.5

Notation: $K_c = (d/d)/c$ and $K_a = (da/dp)a$, where *a* and *c* are the unit cell parameters and *p* is the pressure.

Thus the influence of hydrostatic pressure up to 0.8 GPa on the properties of GLC with HNO_3 (stage 3) and $SbCl_5$ (stage 2) has been investigated.[66,67] Table 2 presents the compressibilities along the *c* and *a* axes for the test compounds as well as the graphite from which the GLC have been synthesised. It is seen from the Table that the compressibility along the *c* axis for the GLC with HNO_3 is greater by a factor of ~1.7 than for the initial graphite, while the compressibility along the *a* axis is much smaller in both cases than along the *c* axis. At the same time, the pressure dependence of the electrical resistance of the GLC with HNO_3 shows an anomaly at 0.5 GPa, which can be related, according to the authors,[66,67] to a structural transition of the compound (however, the nature of this transition is not explained[66,67]). Unfortunately the exact compositions of the compounds investigated are not given in the two studies.[66,67]

The compounds C_8Cs and $C_{36}Cs$ have been investigated by X-ray diffraction at a high hydrostatic pressure (up to 1.2 GPa) and room temperature.[68] The compressibility of C_8Cs along the *c* axis was determined as $K_c = (dc/dp)_{p=0}/c = (1.57 \pm 0.05) \times 10^{-12}$ cm^2 dyn^{-1}, which is much less than the corresponding values for the compounds C_8K (2.1×10^{-12} cm^2 dyn^{-1}) and C_8Rb (2.25×10^{-12} cm^2 dyn^{-1}). The greater "rigidity" of the caesium compound compared with the analogous potassium and rubidium compounds implies, according to the authors,[68] that in this GLC there is marked overlapping of the wavefunctions of the 6s electrons of caesium and the π electrons of graphite along the *c* axis. No pressure-initiated structural transformation was observed for the compound C_8Cs. A reversible phase transformation (with formation of a stage 4 GLC), i.e. a transformation with a change in the stage index of the GLC, was observed[68] in the compound $C_{36}C_S$.

The potassium graphitide C_8K (stage 3) has been studied by neutron diffraction[69] at hydrostatic pressures up to 2 GPa. A reversible phase transition was observed in the pressure range 1.5–1.9 GPa, which leads to the formation of GLC with a non-integral stage index (3/2).

The behaviour of the graphitides C_8M and $C_{12n}M$ (M = Rb or Cs; *n* = 2, 3, 4) has been investigated with the aid of X-ray diffraction and changes in Raman spectra at hydrostatic pressures up to 1 GPa.[70] Pressure-initiated phase transformations with a change in stage index, characterised by reversibility, hysteresis, and a dependence on the nature of the specimen, were observed for all the GLC with $n \geq 2$. The following transitions were noted: GLC (stage 2) → GLC (stage 3); GLC (stage 3) → GLC (stage 4) +GLC (stage 5); GLC (stage 4) → GLC (stage 4) + GLC (stage 5) → GLC (stage 6). It was also observed that the pressure of the transition involving a change in stage index is higher for $C_{24}Cs$ than for $C_{24}K$ and $C_{24}Rb$, which implies, according to the authors,[70] that the repulsive intralamellar interactions are more intense for caesium than for potassium and rubidium (possibly as a consequence of the greater size of the caesium ions). In addition, the compressibilities $K_d = (\partial d/\partial p)_{p=0}/d_0$ where *d* is the packing thickness at a pressure *p* and d_0 the packing thickness at *p* = 0) of the compounds C_8Cs and C_8Rb were measured as $(1.56 \pm 0.05) \times 10^{-12}$ and $(2.42 \pm 0.12) \times 10^{-12}$ cm^2 dyn^{-1} respectively [$K_d = (2.73 \pm 0.09) \times 10^{-12}$ cm^2 dyn^{-1} for the initial graphite and $K_d = (2.13 \pm 0.09) \times 10^{-12}$ cm^2 dyn^{-1} for the analogous potassium compound C_8K].

The compressibility of the stage 1 graphitide C_4KHg has been measured along the *c* axis[71] and has been found to be $(4.4 \pm 0.1) \times 10^{-12}$ cm^{2}dyn^{-1}, which is approximately twice as large as for the analogous stage 1 GLC C_8K, i.e. the compound C_4KHg is much "softer" in the direction of the *c* axis than C_8K. According to Kim et al.,[71] the ternary compound can therefore allow a significant decrease of volume without the formation of ultradense islands of the intercalant and also "corridors", which is the driving force of the pressure-initiated transformations with change of stage index in the compound C_8K.

The stage 1 GLC C_6Li has been investigated by NMR at 232 and 293 K and external pressures $p \leq 0.5$ GPa.[72] It was shown that the quadrupole interaction constant for the graphitide is independent of temperature, but increases linearly (at a rate of 1.5 kHz bar^{-1}) with increase of pressure. The degree of charge transfer to each carbon atom estimated by the authors[72] was −e/12, which agrees with the results of band calculations. The compressibility of the compound C_6Li along the *c* axis, estimated in the above study,[72] was $K_c = 1.7 \times 10^{-12}$ cm^{2}dyn^{-1}, which agrees with the analogous values for the graphitides C_8M (M = K, Rb, or Cs).

A thermodynamic model permitting a satisfactory explanation of, in particular, transitions involving a change in stage index under the influence of high pressure by the formation of GLC with a non-integral stage index at high pressures, and also certain other experimental effects in alkali metal graphitides has been proposed.[73]

A phase transition with a change (non-multiple) in the stage index from two to three has been observed by studying the Shubnikov–de Haas effect for the stage 2 GLC $C_{16}ICl$ at room temperature and a hydrostatic pressure of ~1.2 GPa.[74] A characteristic feature of this transition was a monotonic (in all probability non-threshold as regards pressure) increase of the content of stage 3 regions (having the composition $C_{24}ICl$) and a decrease of the content of the stage 2 regions (having the composition $C_{16}ICl$) with retention of the single crystal nature of the corresponding regions. This transition was explained[74] on the basis of the domain model of the GLC.

The influence of high hydrostatic pressures (up to 2.2 GPa) on the electrical properties of the graphitides C_4KHg (stage 1) and also C_8KHg and C_8RbHg (stage 2) has been investigated.[75–77] Transitions to the superconducting state were observed at atmospheric pressure and temperatures of 1.88 and 1.41 K for the stage 2 GLC C_8KHg and C_8RbHg respectively. The application of hydrostatic pressure lowers the temperature of the transition to the superconducting state at rates of -6.3×10^{-5} and -5.3×10^{-5} K bar^{-1} for the potassium and rubidium compounds respectively.[77]

Results of measurements of the pressure dependence of the temperatures of the transition to the superconducting state for the graphitides C_4MHg and C_8MHg (M = K or Rb) as well as the compounds $C_4KCl_{1.5}$, C_8K, and $C_{24}K$ have been surveyed and discussed.[78–80] It was shown that the electrons in the intercalant zone and not those in the graphite zone play the main role in the superconductivity of materials of the given class and that the two-dimensional anisotropy of the properties of the GLC investigated is important under these conditions.

The influence (at room temperature) of solid-phase pressures (up to 8.5 GPa) on a series of GLC with *d* elements and their chlorides has been investigated[81] and it has been shown that the structures of the compounds investigated do not undergo appreciable changes after their treatment at a pressure up to 8.5 GPa.

We may note that in all the studies discussed above, the influence of high pressures on the properties of various GLC was investigated at room temperature or below room temperature, while the behaviour of the GLC at high pressures and temperatures was not considered, although such data are extremely important and necessary, in particular, in considering the possibilities of the synthesis of artificial diamonds from GLC. The behaviour of a stage 1 GLC with $FeCl_3$ has been investigated under the conditions of quasi-hydrostatic pressures (2–8 GPa) and high temperatures (up to 2000 K) in only one study.[82] It was shown that at $T <$ 700 K the test compound undergoes no changes over the entire experimental pressure range, but it does decompose as the temperature rises with formation of a mixture of higher stage GLC and iron(II) and iron(III) chlorides. On the other hand, the formation of diamonds from the GLC investigated was not observed under the experimental conditions.[82]

IV. THERMAL EXPANSION

The coefficients of thermal expansion (CTE), whose knowledge is especially necessary when the possibility of obtaining artificial diamonds from the corresponding GLC is considered, have been determined in recent years for certain GLC.

The CTE have been measured along the *a* and *c* axes in certain alkali metal graphitides by X-ray diffraction in the temperature range 10–300 K.[83,84] It was shown that the thermal expansion along the *c* axis depends greatly on the density of the arrangement of alkali metal atoms in the interplanar spaces within the GLC and also on the stage index of the compound, being greatest for the potassium graphitide C_8K. It has also been observed that the thermal expansion along the *a* axis of the potassium compounds C_8K and $C_{24}K$ and also of the highly oriented pyrolytic graphite is negative in the experimental temperature range. The results obtained[83,84] are listed in Table 3.

Table 3. The coefficients of thermal expansion along the *a* ($\alpha_\parallel$) and *c* ($\alpha_\perp$) axes of graphite and the GLC with alkali metals.[83,84]

Compound	$\alpha_\parallel \cdot 10^6$, K^{-1}	*T*, K	$\alpha_\perp \cdot 10^6$, K^{-1}	*T*, K
Graphite	0.20	200—280	2.4±0.4	200—300
C_8K	0.40	170—285	4.5±0.8	250—300
$C_{24}K$	0.40	165—280	3.6±0.4	250—300
$C_{36}K$	—	—	3.0±0.6	230—300
C_8Rb	—	—	3.0±0.7	250—300
$C_{24}Rb$	—	—	3.3±0.5	240—300
C_8Cs	—	—	2.8±0.6	240—300

Table 4. The coefficients of thermal expansion of the GLC with sulphuric acid and of graphite.[85]

Stage index*	$10^6\alpha$, K^{-1}	
	83–173 K	223–303 K
1	48.1±1.1	64.7±1.1
2	37.8±0.2	72.3±2.9
3	30.7±0.8	55.3±0.8
4	27.6±1.4	47.7±1.4
Graphite	19.14	25.6

*Only the stage indices of the compounds are indicated in the original communication, but their chemical compositions are not given.

The temperature variation of the repeat period of the GLC with sulphuric acid having four stage indices (from 1 to 4) has been measured by X-ray diffraction in the temperature range 83–303 K.[85] For all the compounds, an anomalous thermal expansion was observed at temperatures from 173 to 213 K, its value gradually diminishing (from 0.097 Å for the stage 1 compound to 0.040 Å for the stage 4 compound). The coefficients of linear thermal expansion α for all the GLC investigated, which proved to be 1.5–3 times greater than the corresponding values for the initial graphite, have been published[85] for two temperature ranges (83–173 and 223 to 303 K). Some of the data obtained[85] are compiled in Table 4 (we may note that, unfortunately, the above communication[85] contains no information about the chemical composition of the test compounds, which to some extent hinders the interpretation of the results).

Vangelisti et al.[86] determined by X-ray diffraction the value of $\alpha_\perp$ for the stage 1 GLC with $AlCl_3$ and $GaCl_3$ and highly oriented pyrolytic graphite and obtained $\alpha_\perp$ $(K^{-1}) = 38.0 \times 10^{-6}$

(in the range ~0–300 K), 29.4 × 10^{-6} in the range ~0–100 K), and 26.5 × 10^{-6} (in the range ~100–300 K).

The structure of the stage 2 GLC $C_{11.3}NiCl_{2.13}$ has been investigated by neutron diffraction and it was found that, when the temperature is raised from 5 to 300 K, the repeat period along the *c* axis increases by 0.078 Å compared with the analogous value (0.071 Å) for the stage 1 GLC with $FeCl_3$. The authors[87] found that at room temperature the CTE of the compound $C_{11.3}NiCl_{2.13}$ is ~4 × 10^{-5} K^{-1}.

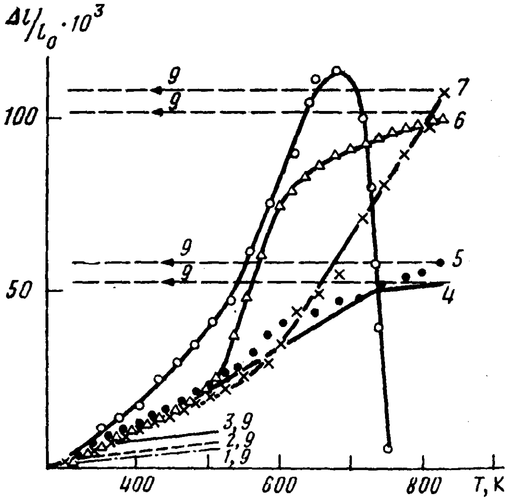

Figure 4. Temperature variation of the relative elongation in the axial direction ($\Delta l/l_0$) of pressed cylindrical specimens of the graphite from the Zaval'evsk deposit (curve *1*), cobalt (curve *2*) and (curve *3*) dichlorides, and the compounds $C_{9.5}CuCl$ (curve *4*), $C_{6.97}CoCl_2$ (curve *5*), $C_{6.35}CuCl_2$ (curve *6*), $C_{16.8}CoCl_2$ (curve *7*), and $C_{7.7}FeCl_3$ (curve *8*) on heating (curves *1–8*) and cooling (curve *9*).[58,59,63,88,89]

Table 5. The coefficients of thermal expansion (α) of certain GLC with metal chlorids.[58,59,63,88,89]

Compound	Stage	$\alpha\cdot10^6$, K^{-1}	*T*, K
$C_{6.35}CuCl_2$	1	9.9	290–440
ditto	1	13.5	450–520
»	1	70.0	530–590
»	1	19.7	600–820
$C_{6.97}CoCl_2$	1	11.7	290–540
ditto	1	26.5	550–590
»	1	8.0	600–800
$C_{16.8}CoCl_2$	2	10.2	300–580
ditto	2	31.1	590–820
$C_{9.5}CuCl$	1	7.2	300–370
ditto	1	14.0	380–715
»	1	1.5	725–820
$C_{7.7}FeCl_3$	1	20.7	310–540
ditto	1	66.7	560–640

We may note that the above studies[83–87] were performed below room temperature and that CTE data in the range above room temperature appeared for the GLC only recently. The results of studies of the characteristic features of the thermal expansion at temperatures up to 820 K for pressed cylindrical specimens of certain GLC (obtained using graphite from the Zaval'evsk deposit) with cobalt(II), copper(II), copper(I), and iron(III) chlorides have been published[58,59,63,88,89] and are summariesed in Fig.4 and Table 5. It is shown that the CTE of the GLC are significantly greater than for the corresponding graphite–salt mixtures, depend on the type of intercalated salt and the stage index of the GLC and are characterised by anisotropy and the possibility of hysteresis. It has been shown[63] that the application of cyclic cold pressing (up to 0.2 GPa) in the formation of cylindrical specimens of the GLC with $Co(Cu)Cl_2$ leads to an increase of the linear CTE and that the influence of such pressing on the stage 1 and 2 GLC is tentative (Fig.5). With increase of the number of the "heating to 523 K–cooling to 300 K–pressing of the specimen until attainment of the initial dimensions" cycle, the linear CTE of the stage 1 GLC diminishes and that of the stage 2 compound increases.

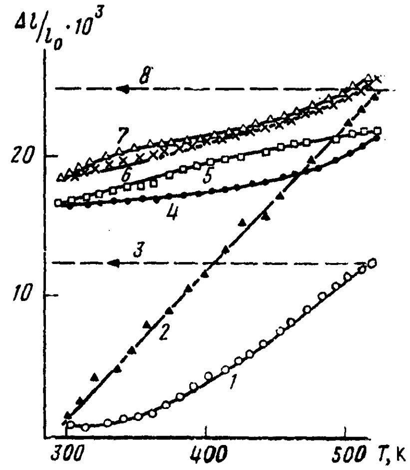

Figure 5. The influence of the previous thermal and baric history on the thermal expansion of the GLC with $CoCl_2$:[63] 1), 2), 4), and 6) heating; 3), 5), 7), and 8) cooling; 1), 3), 6), and 7) $C_{6.97}CoCl_2$; 2), 4), 5), and 8) $C_{16.8}CoCl_2$; "heating–cooling": 6) and 7), 4) and 6) the second and subsequent cycles; "heating–cooling–pressing": 1) and 3), 2) and 8) the fourth cycle.

It has also been established that the process involving the removal from the test compounds of the intercalated components is superimposed on their thermal expansion proper, which in the case of the stage 1 GLC with $FeCl_3$ at a temperature in excess of 660 K leads to the complete breakdown of the initial form of the test specimen.[58,59] It has been suggested that the marked increase in the size of the specimen on heating to 820 K for the stage 2 GLC with $CoCl_2$ compared with the stage 1 compound is probably caused by the preferential alteration of the distances between the carbon networks of the graphite skeleton (in the regions where there is no intercalated component) in the stage 2 GLC as a consequence of the decrease of the electron density caused by the donor–acceptor interaction between the carbon layers and the cobalt chloride (the carbon layers function as electron donors), while the distance between the carbon layers and the salt in the GLC with $CoCl_2$ corresponding to both stage indices increases to a lesser extent.

V. THERMAL STABILITY

Despite the great practical value of data on the thermal stability of GLC, for the majority of them (even for the compounds with $FeCl_3$ which have been most thoroughly characterised from this standpoint[20–27]), the question of their behaviour on heating has not been finally solved.

The behaviour of GLC with homogeneous (1) and mixed (1 + 2) stage indices having the composition graphite + $FeCl_{3-y}$ (where $0 \leq y \leq 1$) on heating has been investigated by Raman spectroscopy[90] and it was found that after the compounds had been kept at 648 K, a fraction of the stage 3 compound appeared. The increase of y (i.e. of the fraction of intercalated $FeCl_2$) after heating was also confirmed by measuring the Mössbauer effects.

An isobaric thermoanalytical investigation of the decomposition processes in nitrogen, helium, and argon atmospheres of GLC with $FeCl_3$ corresponding to stage 1 (C_6FeCl_3) and 2 ($C_{12}FeCl_3$) has been carried out in the temperature range 298–750 K and in the pressure range 10–700 mmHg.[56] It was shown that the thermal decomposition of these compounds takes place in steps. Thus at a low pressure the stage 1 compound decomposed in two steps:

$$\text{GLC (stage 1)} \rightarrow \text{GLC (stage 2)};$$

$$\text{GLC (stage 2)} \rightarrow \text{graphite} + FeCl_3.$$

At higher pressures the thermograms showed a single peak which the authors assigned[56] to the process

$$\text{GLC (stage 1)} \rightarrow \text{graphite} + FeCl_3.$$

We may note that the formation of GLC with $FeCl_2$ or $FeCl_2$ was not observed[56] in the decomposition of the compounds investigated, which conflicts with the results of other studies.[22,24,57–60,90]

In a DSC study of GLC with titanium(IV) and tin(IV) chlorides corresponding to different stage indices showed that, regardless of composition, these compounds decompose below room temperature—near the melting point of the corresponding pure intercalated component (249 K for $TiCl_4$ and 240 K for $SnCl_4$).[48,49]

The behaviour of the stage 2 GLC with aluminium bromide, having the composition $C_{20.8}AlBr_{3.5}$, has been investigated by differential thermogravimetric analysis (heating to 1173 K at a rate of 10 K min^{-1} in an atmosphere of dry nitrogen and a pressure of 10^5 Pa) (Fig.6).[91] The specimen lost mass in three stages: 1) initially (at 343–473 K) the excess bromine was probably lost (weight loss 7%); 2) next there was a stepwise transition from the stage 2 compound to one corresponding in terms of its composition to stage 6 (at 693 K the weight loss was 38.5% and the rate of decomposition slowed down sharply); 3) on further heating to 1173 K, the weight loss reached 43–47% (on the other hand in the case of the complete decomposition of the substance, the weight loss of the specimen should be 55%). The authors explained this[91] by the low rate of desorption of the GLC decomposition products, the relatively short decomposition time, and also the formation of a residual graphite compound.

The thermal behaviour of the graphitides C_4KHg and $C_4KTl_{1.5}$ has been studied[92] and proved to be significantly different for the two compounds. Thus the melting points of the pure alloys and the alloys intercalated in graphite and having the same composition were found to be 449 for KHg, ~673 K for KHg in C_4KHg, ~593 K for $KTl_{1.5}$, and ~603 K for $KTl_{1.5}$ in $C_4KTl_{1.5}$. This enabled the authors[92] to assume, in conformity with crystallographic data, that the interaction between the layers of the intercalated "alloy" and the neighbouring layers of the graphite is much weaker for thallium compounds than for mercury compounds.

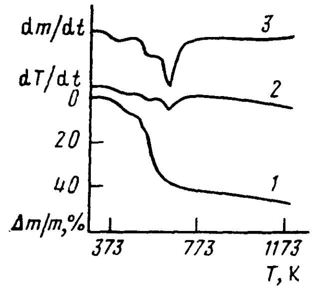

Figure 6. Thermal analysis curves for the compound $C_{20.8}$.$AlBr_{3.5}$: 1) weight loss by the specimens; 2) DTA; 3) DTA.[91]

The results of an investigation of GLC with metal fluorides having the compositions $C_9F(MgF_2)_{0.08}$, $C_{11}F(MgF_2)_{0.14}$, and $C_{11}F(AlF_3)_{0.09}$ and also of the graphite fluoride $(C_2F)_n$ by differential thermal analysis in air have been published.[93] Starting from 463 K, a broad exothermic peak was observed for the compounds $C_x(MgF_2)_y$ (the decrease of the weight of the specimen began at the same temperatures). For the compound $C_{11}F(AlF_3)_{0.09}$, the broad exothermic peak began at 503 K. The authors did not elucidate the nature of these peaks.[93] The peaks near 1103 K, which were observed for all three compounds, were assigned to the oxidation reaction of the graphite residue. For the graphite fluoride, two exothermic peaks were noted at 846 and 970 K, the first corresponding to the decomposition of the compound and the second to the oxidation of the residual carbon.

The decomposition in air of mixed GLC with uranium hexafluoride and Freon 113, having the composition $C_n[UF_6$.(Freon 113)], has been investigated by thermogravimetric analysis.[94] It was found that the ternary compound decomposed in four stages: (1) at 313–473 K; (2) at 448–523 K; (3) at 473–723 K; (4) at 703–988 K. The graphite fluorination products with intercalated UF_6 molecules are obtained in the first three decomposition stages (analogous products are formed on thermal decomposition of the GLC with UF_6) and uranium is not removed from the compound. During the fourth (exothermic) stage, the residual Freon is evolved with simultaneous loss of carbon, which is proportional to the uranium content. The amount of Freon in the initial GLC and the intermediate products of their decomposition is not correlated with the uranium content but is proportional to the amount of graphite. In the most stable intermediates, formed after the third decomposition stage, there are approximately 12 carbon atoms per Freon 113 molecule.

The removal of ammonia from the ternary GLC $C_{12}M(NH_3)_2$ (where M = lithium, sodium, potassium, rubidium, caesium, calcium, strontium or barium) has been investigated by chemical analysis and X-ray diffraction.[95] In terms of their behaviour as regards the elimination of ammonia, the GLC were classified[95] in three groups: (1) GLC with caesium and rubidium, from which the entire ammonia is removed; (2) GLC with sodium and potassium, which also evolve most of the ammonia and are themselves converted into new GLC; (3) GLC with lithium and alkaline earth metals, which give rise to amides on decomposition and the decomposition process itself is extremely complex.

It has been shown[96] that the graphite compounds $C_2F.yEFn.zR$ of a new type, which have the cage structure (the molecules of the fluoride in them are, as it were, located in cages formed by the carbon layers and fluorine atoms), exhibit a fairly high (in our view) thermal stability (up to 573–673 K). It has been established by differential thermal analysis (DTA) that the compound $C_2F.0.35BrF_3.0.17SnF_4$ decomposes at 553–623 K in several stages (although the stages themselves have not been described). It has been shown[98] that the GLC $C_{10.3}MoF_6$ is stable up to 523 K and the compound $C_{53.7}.WF_6$ is stable up to 503 K, both GLC decomposing on heating to 823 K with formation of pure graphite.

Studies on the graphite compounds $(CF_{0.97}.0.05HSO_3F)_n$ and $(CF_{1.23-1.25})_m$ showed[99] that their thermal stability depends both on the type of the initial graphite and on the conditions under which the compounds are obtained, varying in the range from 533 to 733 K. It has been shown with the aid of DTA[100] that, on heating to 373 K, hydrogen fluoride is evolved endothermically from the compound $C_xF.yNO_3.zHF$, while in the temperature range 623–673 K the complete exothermic decomposition of the compound takes place. The thermal stability of the compounds $[C_xF_y(NH_2)_z]_n$ and $C_xF_x.Cl_y.zN_2O_4$ has been investigated[101] and it has been shown that the graphite aminofluorides are thermally stable up to 373 K, and that their decomposition involves the formation of carbon, nitrogen, and hydrogen fluoride. When the compound $C_xF_yCl_y.zN_2O_4$ is heated to temperatures in the region of ~473 K, NO_2 is evolved into the gas phase (but the composition of the solid residue was not indicated). A definite correlation has been observed[102] between the thermal stability of graphite fluorides (according to DTA data) and the interplanar spacing in these compounds: the temperatures of the onset of decomposition are higher for compounds with a smaller interplanar spacing.

In a study of the thermal stability of the graphite oxide fluoride $C_8O_{0.8}F_{3.6}$,[103] two exothermic effects were observed on the derivatogram: at 453 K (this peak is characteristic of oxygen-containing graphite compounds) and at 673 K (graphite fluorides normally decompose in this temperature range). The mass spectrum of the gaseous decomposition products of the compound revealed the presence of the ion CF^+, CF_2^+, CF_3^+, COF_2^+, CO^+, and CO_2^+. The thermal stability of GLC with metal fluorides having the composition C_8MoF_5, $C_{22.9}.NbF_5$, and $C_{13.6}TaF_5$ has been investigated[104] and it has been shown that the compound C_8MoF_5 decomposes in the temperature range 443–608 K. The decomposition is accompanied by a large number of superimposed exothermic and endothermic effects, which can be explained, according to the authors,[104] by the disproportionation of the intercalated MoF_5. In the decomposition of other GLC, a smooth weight loss was observed in the temperature ranges 673–763 K (for $C_{22.9}.NbF_5$) and 563–683 K (for $C_{13.6}TaF_5$); in this case there was apparently no disproportionation of NbF_5 and TaF_5.

Lisitsa et al.[105] investigated the amino-derivatives of graphite $C_3O(NH_2)_{1.3}$ and $C_3(NH)_{1.3}$ and found that the former compound is almost fully converted into volatile products in the region of 673 K in an inert atmosphere. According to mass-spectrometric data, the compound $C_3(NH)_{1.3}$ is stable up to 573 K, decomposing in the region of 773 K with evolution of gaseous hydrogen cyanide, ammonia, and hydrogen. It has been demonstrated by ^{19}F NMR[106] that reversible disproportionation of ClF_3 with formation of ClF and ClF_5 takes place within the crystal structure of the compound $C_{3.65}.F_{2.17}Cl_{0.42}$. With the aid of derivatographic studies of the carbon fluorides $(CF_x)_n$, it has been shown[107] that, depending on the fluorine content and the conditions in the preliminary treatment of the specimens, the temperature of the onset of their decomposition is in the range 543–653 K and the maximum rate of decomposition is attained at temperatures in the range 753–833 K. A relation between the structure of the initial carbon material and the thermal stability of fluorocarbon materials has also been noted in another investigation;[108] fluorination of materials with a more ideal structure yielded specimens with a lower thermal stability.

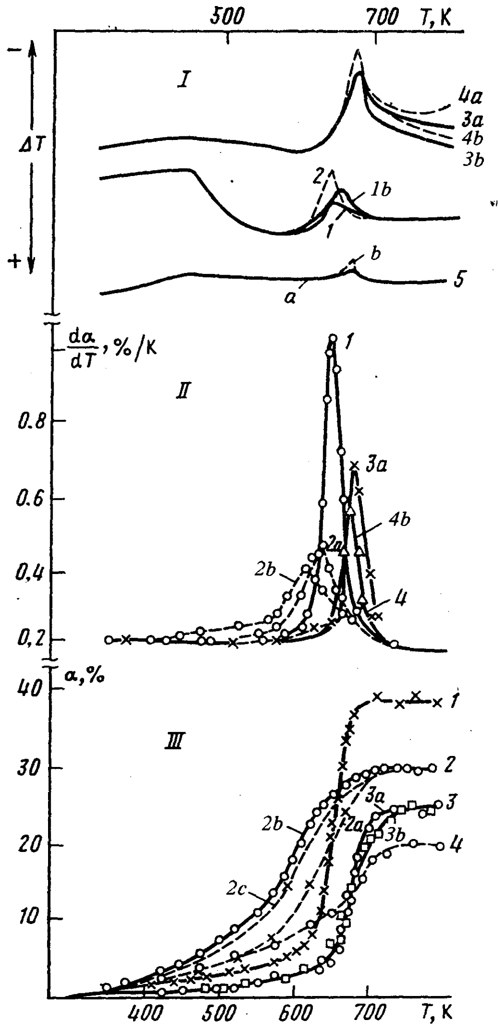

Figure 7. DTA (I), DTG (II), and TG (III) curves for $C_{7.7}FeCl_3$ (curves *1*, *3*, and *5a*) and $C_{11.83}FeCl_3$ (curves *2*, *4*, and *5b*) *in vacuo* (curves *1* and *2*), in air (curves *3a* and *4a*), in argon (curves *3b* and *4b*), and in a sealed tube (curve *5*), the specimens (30 mg) having particle sizes ≤0.25 mm curves *1*, *2a*, and *2b*) and 0.25–0.5 mm (curves *1b* and *2b*), at heating rates of 1 K min^{-1} (curves *2b* and *2c*) and 5 K min^{-1} (curves *1*, *2a*, and *3–5*) α is the degree of conversion of the specimen).[58,59]

The thermal decomposition of the compound $C_{16.1}BrF_{9.3}$ has been studied[109] with heating at a rate of 10 K min^{-1} in argon and with the specimen kept for 1 h in nitrogen at 513, 573, and 713 K. It was shown that the decomposition takes place stepwise. Processes involving the oxidative fluorination of the graphite skeleton and leading to the expansion of the lattice in the direction of the c axis take place in the first stage. The new phase is formed in the second stage (at 713 K and above) and decomposes destructively at 833–863 K and above with formation of gaseous fluoro-derivatives of carbon having unsaturated and saturated compositions[110] and also an amorphous carbon residue.

Table 6. The energy characteristics (the apparent activation energies E_a, the enthalpies ΔH, and the entropies ΔS) of the solid-phase transformations and the enthalpies of thermal decomposition along the section E–F (ΔH^*) in the thermostimulated processes in GLC.[57–60,111–114]

Compound	Medium	E_a, kJ mol^{-1}		Solid phase transformations		ΔH^*, kJ mol^{-1}
		section C-D	section E-F	ΔH, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}	
$C_{6,8}FeCl_3$ (stage 1)	sealed tube	—	—	—	—	14.4
	air (argon)	—	—	—	—	85
	vacuum	—	—	—	—	93
$C_{7,7}FeCl_3$ (stage 1)	sealed tube	—	—	0.13±0.03	0.3±0.1	—
	vacuum	4,4±0.7	26±4	—	—	—
$C_{11,83}FeCl_3$ (stage 2)	sealed tube	—	—	2,78±0.41	6.1±1.2	19.5
	air (argon)	—	—	—	—	94
	vacuum	12.2±1.8	32.4±4.2	—	—	106
$C_{6,35}CuCl_2$ (stage 1)	vacuum	—	23±1	—	—	—
$C_{7,73}CuCl_2$ (stage 1 and 2)	sealed tube	—	—	—	—	75
	air (argon)	—	—	—	—	115
	vacuum	—	29±2	—	—	170

Note. The sections are indicated in Fig.8 and have been assigned to definite thermoinitiated processes.

A number of studies[57–60,111–114] have been devoted to the investigation of the kinetics, thermodynamics, and mechanism of the pyrolysis of GLC and layered compounds of carbon fibres (LCCF) with iron(III), copper(II), and other metal chlorides by dynamic thermogravimetric measurements (TG), quantitative DTA combined with X-ray diffraction and chemical analysis, time of flight mass spectrometry, and Mössbauer spectroscopy. It was shown that the GLC with $CuCl_2$ ($FeCl_3$) begin to undergo thermal decomposition at relatively low temperatures (460–500 and 320–350 K respectively) and that the physicochemical parameters of the linear pyrolysis depend on a number of experimental factors: the degree of dispersion of the GLC particles, the mass of the sample, the rate of heating of the specimens, the gaseous environment (vacuum, inert gas, air), the external pressure, and the nature of the carbon matrix [Zaval'evsk graphite, carbon fibres based on cellulose hydrate, polyacrylonitrile (PAN), etc.] (Figs.7–11 and Table 6). When the GLC are heated, hydrogen chloride and water, present in the materials (at the defects in the graphite skeleton and at the edge molecules of the intercalated chlorides) by virtue of the methodological features of the synthesis,[115] are removed initially (section A–B in Fig.8 corresponds to this process for the GLC with $FeCl_3$). It was found that the stage 2 GLC have a somewhat higher thermal stability than the stage 1 compounds, but that their main thermal degradation occurs approximately within the same temperature limits as for the pure salts, which indicates a low strength of the bond between the layers of the graphite matrix and the intercalated component. On passing from GLC to LCCF, the thermal stability of the compounds falls somewhat, being lower for the LCCF based on a cellulose hydrate than for the LCCF based on PAN (cf.Figs.9 and 11). It was established that, when the GLC with $FeCl_3$ is heated to 800 K, $FeCl_3$ ... # from them at $T > 370$ K (section C–D in Fig.8), while at higher temperatures $FeCl_3$ dissociates in the interplanar space within the graphite skeleton into $FeCl_2$ and in Cl_2 with formation of a GLC with $FeCl_2$ and the removal of Cl_2 (section E–F in Fig.8). This conclusion agrees with other data[22,24,90,116,117] but conflicts with the results of Solozhenko et al.[56] The possible causes of the discrepancies between the two sets of data in Refs.57–60 and 56 may be, in particular, different experimental conditions, different type and degree of dispersion of the initial graphite, etc.

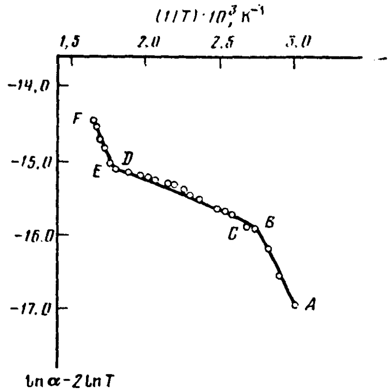

Figure 8. A typical form of the dependence of $\ln\alpha - 2\ln T$ on $1/T$ for the linear pyrolysis *in vacuo* of the GLC with $FeCl_3$ used[58,59] to estimate the apparent activation energies.

Several studies of the properties of LCCF have been published in recent years. Oshima et al.[118] obtained LCCF with $CuCl_2$, consisting of a mixture of stage 1 and 2 compounds, and demonstrated by electrical resistivity measurements that the LCCF with $CuCl_2$ are stable in air up to 450 K.

The compounds formed on interaction of gaseous fluorine and lithium fluoride with graphite materials of different nature (natural and pyrolytic graphite as well as carbon fibres) and having the composition $C_xF(LiF)_y$ (where x and y are 9–13 and 0.1–0.002 respectively for graphite) have been investigated by X-ray diffraction, ^{19}F NMR, thermogravimetric analysis (TGA), and conductimetric measurements.[119] The thermal stability in air was a maximum for the compounds obtained from carbon fibres: the LCCF decomposed at 680 K (a decrease in mass and an endothermic reaction were recorded at this temperature), while the compounds based on natural graphite decomposed at 537 K. We may note that, after

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#Misprint in Russian text (Translator).

prolonged exposure to air at room temperature, the specimens obtained from carbon fibres underwent reversible changes (manifested, in particular, by a decrease of their resistivity).

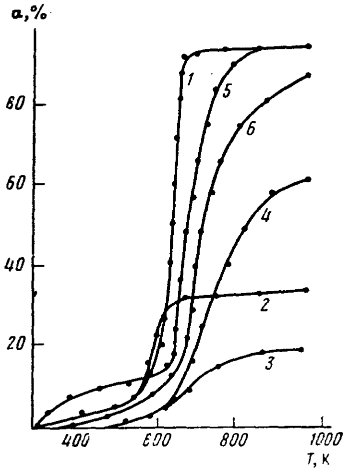

Figure 9. TGE curves for $CuCl_2$ (curve *1*) and LCCF with $CuCl_2$ based on viscose (curves *2* and *5*) and PAN (curves *3–6*) and the compound $C_{6.35}CuCl_2$ (curve *4*) *in vacuo* (curves *1–4*) and in air (curves *5* and *6*); α is the degree of decomposition of the test specimen; heating rate 5 K min^{-2}.[112]

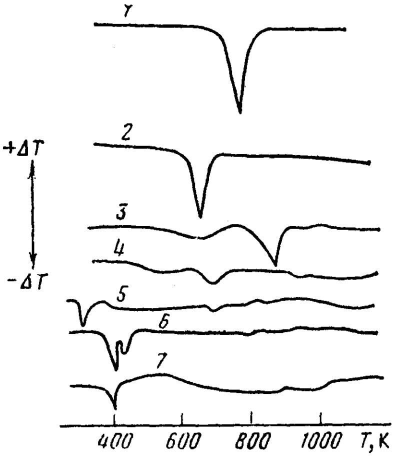

Figure 10. DTA curve for $CuCl_2$ (curves *1* and *2*), the compound $C_{6.35}CuCl_2$ (curves *3* and *4*), and the LCCF with $CuCl_2$ [based on viscose (curves *5* and *7*) and PAN (curve *6*)] *in vacuo* (curves *2*, *4*, and *5*), in argon (curves *1*, *3*, and *6*), and in air (curve *7*); heating rate 5 K min^{-1}.[112]

By measuring the temperature variation of the resistivity of LCCF with $FeCl_3$ and $CuCl_2$ ($4 < T < 600$ K), Endo et al.[120] showed that the desorption of the intercalated component from the compound is not observed up to ~513 K (for $CuCl_2$) and 613 K (for $FeCl_3$). It was also found that both LCCF are stable in air. A LCCF with potassium has been synthesised[121] and its electrical properties have been investigated. The authors[121] established the formation of compounds with different stage indices in the case of the LCCF and also found that the LCCF with potassium undergo the same phase transformations as the layered compouds of potassium with synthetic graphite, although the transition temperature and the rate of transformation can differ for different materials.

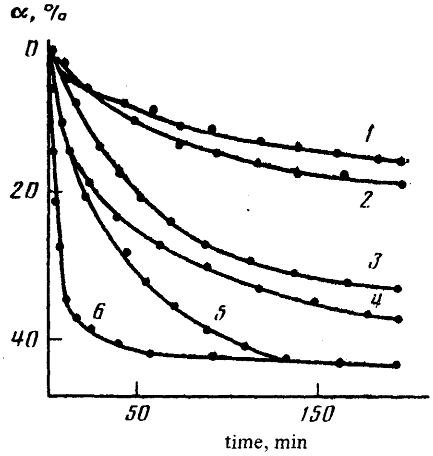

Figure 11. Dependence of the degree of decomposition (α, %) of specimens of the LCCF with $CuCl_2$ based on viscose (curves *1*, *2*, *5*, and *6*) and the compound $C_{6.35}CuCl_2$ (curves *3* and *4*) on the duration of their heat treament *in vacuo* at different temperature (K): 1) 523; 2) 548; 3) and 5) 573; 4) and 6) 623.[112]

The intercalation of certain strong acceptors (AsF_5, SbF_5, SO_3, and HSO_3F) and their mixtures in carbon fibres and the electrical properties of the resulting LCCF have been studied.[122] It was shown that the LCCF with AsF_5, enclosed in a Teflon envelope, retained their thermal stability up to 373 K. Natarajan et al.[123] investigated the electrical properties of LCCF with ICl, Br_2, and $CuCl_2$ and showed that the LCCF with $CuCl_2$, which are stable in air, retain their themal stability up to 373 K. Dziemianowicz and Forman[124] investigated the properties of LCCF with certain acceptors (nitric acid, $AlCl_3$, and $FeCl_3$). It was noted that both chlorides form LCCF with different stage indices. In contrast to the data of Endo et al.,[120] Dziemianowicz and Forman[124] noted that the LCCF with $AlCl_3$ and $FeCl_3$ are extremely unstable in air (they are rapidly and irreversibly hydrated and drying of the hydrated product does not lead to the reformation of the initial LCCF).

In the above studies the compounds were investigated under the usual pressure. Solozhenko and Kalashnikov[82] investigated the behaviour of GLC with $FeCl_3$ at high pressures (2 to 8 GPa) and temperatures (300–2000 K) showed that the observed decomposition reactions of the stage 1 compound can be described by means of the scheme

$$\begin{tikzcd}
\text{GLC with } FeCl_3 \text{ (stage 1)} \arrow[r] & \text{GLC with } FeCl_3 \text{ (higher stages)} \arrow[d] & + FeCl_3 \arrow[d, shift left] \\
 & FeCl_3 + \text{C(graphite)} & FeCl_2 + 0.5Cl_2 \arrow[u, shift left]
\end{tikzcd}$$

As was in fact suggested by the authors,[82] the decomposition of the GLC with $FeCl_3$ at high static pressures and temperatures then proceeds via a qualitatively different mechanism than in the case of high dynamic pressures.

We may note that, according to a number of data,[61,125,126] the removal of the intercalated components of the GLC does not necessarily require heating and has been observed for a number of compounds even at room temperature. Thus Hwang et al.[125] investigated the behaviour of the stage 1 compound C_8Cs, whilst it was maintained *in vacuo* (10^{-9} mmHg, room temperature) for a week. It was shown that caesium is removed from the GLC, which leads to the appearance of a multiphase structure in which the size of the domains is ~1 μm. By measuring the Mössbauer effect, it was demonstrated[126] that, after prolonged (up to 1 year) exposure to air of the specimens of the GLC with $FeCl_3$ corresponding to stage indices, the following phenomena were observed: an appreciable decrease of the iron content [and hence of iron(III) chloride] in the specimens; in the case of the specimens containing a certain number of vacancies, $FeCl_3$ was converted into the $FeCl_4^-$ ions; after the formation of the $FeCl_4^-$ ions, the GLC specimens with individual stage indices were converted into disordered substances.

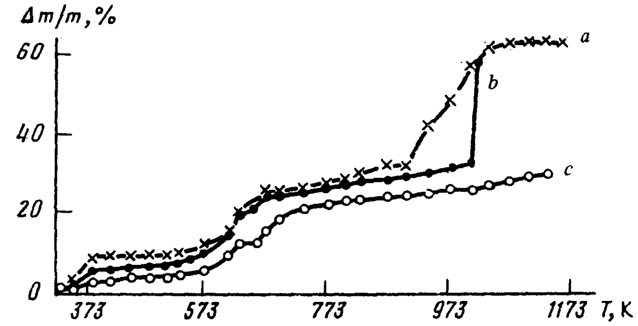

Figure 12. TGA curves for the GLC with $FeCl_3$: *a*) freshly prepared; *b*) after storage in air; *c*) after storage (the maximum weight loss for the stage 1 GLC is 65%).[61]

An extensive study of the behaviour of the GLC with $FeCl_2$ and $FeCl_3$ under different conditions (in particular, during storage, heating, and treatment with water and various solvents) has been carried out[61] by the gravimetric, X-ray diffraction, electron microscope, and Mössbauer spectroscopic methods[61] (Fig.12). Two main types of processes were observed: a gradual conversion of the initial compound into GLC with higher stage indices or direct removal of the component intercalated in the graphite skeleton. A mechanism of the possible reactions occurring when the GLC are kept in air for a long time (up to 40 days) was put forward[61] and it was shown that the products of the decomposition of the compound are iron(II) and iron(III) chloride hydrates and oxide hydrates, disordered graphite, etc.

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It is seen from the results presented above that, despite the apparently large number of data on the physicochemical properties of GLC which have been published in recent years, there are no systematic data of this kind for the majority of the compounds.

A future systematic study of the physicochemical properties of GLC over a wide range of temperatures and pressures will be necessary and it will be desirable to carry out a simultaneous combined study of various properties on identical specimens, since it has been demonstrated that many properties of GLC depend on the previous history of the specimens (in particular, on the duration and conditions of their storage). The latter factor makes it necessary to approach the comparison of data obtained by different investigators with much caution and makes it essential to take into account the form of the graphite matrix in the compound.

Unfortunately, there are very few data on the thermophysical and thermodynamic properties of GLC, the need for which (especially for accurate data) is great. It is desirable that the relevant communications should present the results of the chemical analysis of the compounds (and should not simply indicate the stage index of the GLC, as is being done at the present time in many investigations), because certain properties of GLC depend on whether the given compound is saturated or unsaturated. The lack of information about the formula composition of the test substances frequently makes it difficult to both interpret the data obtained and to compare the results of different investigations with one another. The accumulation of reliable data on the physicochemical properties of GLC will permit further progress in the elucidation of the relation between their structure and properties.

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Nitroxy-radicals in the Liquid-phase Oxidation Reactions of Organic Compounds

S.A.Maslov and G.E.Zaikov

The review is devoted to the mechanism of the action of stable nitroxy-radicals in liquid-phase oxidation reactions of organic compounds. The chemical reactions which take place with participation of nitroxy-radicals are examined and their kinetic parameters are presented. The causes of the high inhibition coefficients and the possible ways of regenerating the nitroxy-radicals from their reaction products are discussed. The phenomenon of the selective inhibition of polymerisation processes accompanying oxidation is described and the conditions necessary for selective inhibition and the possibility of using nitroxy-radicals for this purpose are discussed.
The bibliography includes 97 references.

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I. INTRODUCTION

Stable nitroxy-groups are nowadays finding increasing application in various branches of scientific research and in industrial practice. In particular, they are used as stabilisers in the storage of organic substances, as spin labels and paramagnetic probes in molecular biophysics, and as acceptors and counters of free radicals in the study of the mechanisms of chemical reactions. Numerous data concerning the ways of preparation, properties, and applications of nitroxy-radicals have been published.[1–7] The principal characteristic of nitroxy-radicals, which distinguishes them from other stable organic radicals, is the absence of delocalisation of the unpaired electron.[1,8]

One of the causes of the great interest shown in nitroxy-radicals is that they are effective stabilisers of the oxidative degradation and photodegradation of polymers, in the first place polyolefins.[9–20] The characteristic features of the action of nitroxy-radicals as UV-stabilisers of polymeric materials have been examined in detail,[11,14] but much less attention has been devoted to problems of their antioxidant stabilisation. It is known that many processes occurring in polymers can be successfully investigated using simpler reactions with participation of low-molecular-weight substances, for example, monomers, as models. The study of the mechanism of the action of nitroxy-radicals in the oxidation of monomers is of interest also from this point of view. The criteria of the applicability of such monomeric models to the solution of problems in the field of the degradation and stabilisation of polymers have been formulated.[9,21–23]

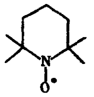
This review is devoted to the action of nitroxy-radicals in the liquid-phase oxidation reactions of monomeric organic compounds which make it possible to obtain many important products of organic synthesis. Fairly numerous interesting results exist in this field but hitherto they have not been surveyed or described systematically. The review deals with the principal experimental data obtained in the study of the reactions of nitroxy-radicals in chain oxidation processes during the last 20–25 years, i.e. virtually since the inception of this field of research. This led to a number of generalisations and certain mathematical relations describing the action of nitroxy-radicals in oxidation systems are given.

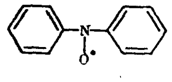
II. CHEMICAL REACTIONS WITH PARTICIPATION OF NITROXY-RADICALS IN OXIDATION REACTIONS OF ORGANIC COMPOUNDS

Stable nitroxy-radicals are able to inhibit radical chain processes. The inhibiting effect of nitroxy-radicals is due to the fact that they are able to enter into reactions, involving the saturation of the valence, with other species having an unpaired electron, in particular with free organic radicals propagating the oxidation chain.

For an oxidative chain reaction, it is possible to determine even from concentration relations which of the radicals, the alkyl radical $R^{\cdot}$ or the peroxy-radical $RO_2^{\cdot}$, participates in chain termination (i.e. in recombination by adding to the nitroxy-radical). If the chain of oxidation depends on the partial pressure of O_2 in the system, this means that the radicals $R^{\cdot}$ are responsible for the chain termination. When the rate of reaction is independent of the oxygen content, the $RO_2^{\cdot}$ radicals are responsible for chain termination. Another way of determining the nature of the termination consists in the identification of the termination product by chemical and spectroscopic methods.

It has been established unambiguously that heterocyclic and aliphatic† nitroxy-radicals, in particular radicals of the piperidine series having the general formula (I), react solely with the alkyl radicals $R^{\cdot}$ and do not interact with the peroxy-radicals $RO_2^{\cdot}$.


(I)
2,2,6,6-Tetramethylpiperidin-1-yloxy-radical


(II)
Diphenylnitroxy-radical

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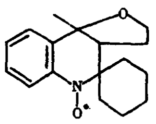
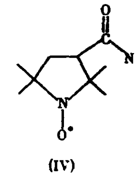
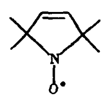
† All these non-aromatic radicals will henceforth be referred to for brevity simply as heterocyclic radicals.



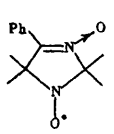
(III)
4-Methyl-2-spirocyclohexyl-3,4,2′,3′-tetrahydrofurano-1,2,3,4-tetrahydroquinolin-1-xyloxy-radical



(IV)
3-Carbamoyl-2,2,5,5-tetramethylpyrrolidin-1-yloxy-radical



(V)
2,2,5,5-Tetramethylpyrrolin-1-yloxy-radical



(VI)
2,2,5,5-Tetramethyl-4-phenyl-3-oxoimidazolin-1-yloxy-radical

This was demonstrated in the oxidation of ethylbenzene,[24,25] polyethylene and polypropylene,[26] and cumene and cyclohexyl methyl ether,[27] in the radiolysis of organic compounds,[28,29] and in the decomposition of azoisobutyrodinitrile.[30] It has been established that, in the radiolysis of water,[31] the nitroxy-radicals (VI) of the imidazoline series react with H atoms and with a hydrated electron but do not react with the $HO_2^{\cdot}$ radical. Fig.1 illustrates the reactivity of heterocyclic nitroxy-radicals. It is seen that, in an atmosphere of oxygen, where the $RO_2^{\cdot}$ radicals propagate the oxidation chain, the nitroxy-radical (I) is not consumed in the oxidation of ethylbenzene. The stationary concentration of the $RO_2^{\cdot}$ radicals, characterised by the chemiluminescence intensity (I/I_0), then also remains unchanged.

In the oxidation of many compounds, especially aromatic hydrocarbons, the stationary concentration of peroxy-radicals is much higher than the concentration of the alkyl radicals $R^{\cdot}$, as a result of which the heterocyclic nitroxy-radicals cannot be effective inhibitors of such reactions. On the other hand, in the oxidation of olefins characterised by relatively high concentrations of the radical $R^{\cdot}$, the inhibition of the reaction by heterocyclic nitroxy-radicals has been observed. As an illustration, Fig.2 presents the kinetic curves for the liquid-phase oxidation of hex-1-ene inhibited by a nitroxy-radical of type (I).[32] An analogous picture has been observed in the oxidation of β-carotene (a polyene).[33]

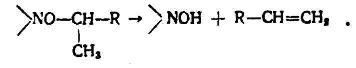
The interaction of heterocyclic nitroxy-radicals with alkyl radicals results in the formation of the corresponding hydroxylamine ethers:[29,34–36]

$$>NO^{\cdot} + R^{\cdot} \xrightarrow{k_a} >NOR\ .$$

The disproportionation reaction is also possible:

$$>NO^{\cdot} + R^{\cdot} \xrightarrow{k_b} >NOH + \text{olefin}.$$

According to Berger et al.,[30] the ratio $k_b/k_a = 0.21$ for the nitroxy-radical (I) and the radicals $(C_6H_5)_2\dot{C}(CH_3)$ and does not change over the range 60–80 °C. In the presence of hydrogen atoms in the α-position, a decomposition reaction can occur,[37,38] for example:



$$>NO{-}\underset{\large CH_3}{CH}{-}R \rightarrow >NOH + R{-}CH{=}CH_2\ .$$

In an acid aqueous medium, hydroxylamine ethers are capable of being deprotonated and of dissociating:[29]

$$>NOR + H^+ \rightarrow -\overset{+}{N}HOR\ ;$$

$$-\overset{+}{N}HOR \rightleftarrows >\bar{N}OR + H^+_{aq}\ .$$

The pK_a for the equilibrium depends on the nature of the radical R and the nitroxy-radical.

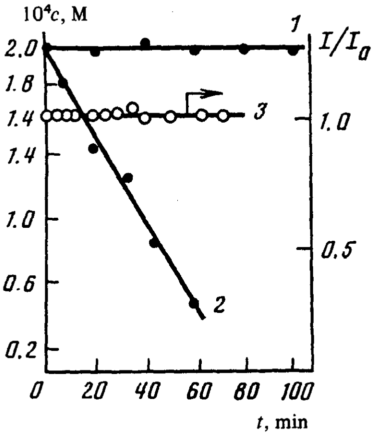


Figure 1. The time (t) variation of the concentration of type (I) nitroxy-radicals (c) in ethylbenzene at 60 °C with the solution bubbled with air (line *1*) and helium (line *2*) and variation of the relative intensity of chemiluminescence (line *3*) under the same conditions for the solution bubbled with air.[25]

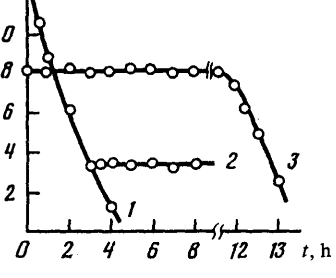
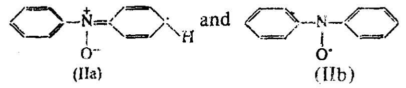


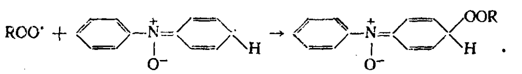
Figure 2. Kinetic curves for the consumption of hex-1-ene during its oxidation with air in acetone (145 °C, 50 atm):[32] 1) without inhibitor; 2) in the presence of 3×10^{-3} M 4-hydroxy derivative of the radical (I); 3) in the presence of 5.2×10^{-4} M 4-hydroxy derivative of the radical (I).

Aromatic nitroxy-radicals, for example, the radicals (II) of the diphenylamine series, can react not only with the radicals $R^{\cdot}$ but also with $RO_2^{\cdot}$. Nitroxy-radicals of type (II) can exist in two forms:[39,40]

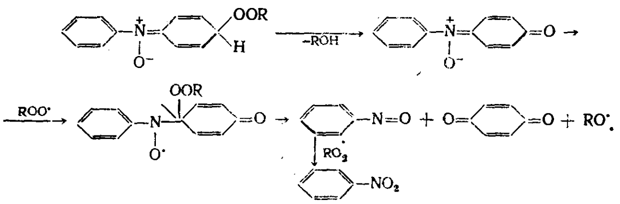


(IIa) (IIb)

The radicals $RO_2^\cdot$ are destroyed with participation of the mesomeric form (IIa), which can be represented as follows:[24,39]



This reaction is accompanied by the irreversible consumption of the nitroxy-radical via the mechanism:



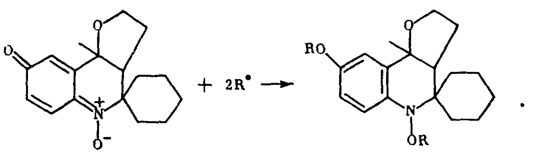
(1)

It has been suggested[41] that the nitroxy-radical (II) interacts with the $RO_2^\cdot$ radical as follows:

$$>NO^\cdot + C_nH_{2n+1}O_2^\cdot \xrightarrow{k_b} >NOH + O_2 + C_nH_{2n}\,. \qquad (2)$$

When cumene is heated in the absence of oxygen but in the presence of an initiator, namely azobisisobutyrodinitrile (AIBN), the aromatic nitroxy-radical (II) reacts with the radicals $R^\cdot$, forming a hydroxylamine ether, as in the reaction involving heterocyclic nitroxy-radicals.

According to Lobanova and co-workers,[42,43] the spiran nitroxy-radical (III) also interacts not only with alkyl but also with peroxy-radicals. The quinone-nitrone formed in the latter case does not react further with $RO_2^\cdot$, but functions as an acceptor of alkyl radicals:



The nitroxy-radical (III) is capable of reacting also with alkoxy-radicals $RO^\cdot$, but the product formed has not been identified. On the other hand, it does not react with phenoxy-radicals.

The reactions of nitroxy-radicals with other free radicals, formed in the oxidation of alcohols and amines, are distinguished by certain characteristic features. Both "alkyl" and peroxy-radicals derived from alcohols and amines can be destroyed by any nitroxy-radicals[44,45] and the reaction product is not an ether but the corresponding hydroxylamine itself:

$$>NO^\cdot + HO{-}\dot{C}< \;\rightarrow\; >NOH + O{=}C<\,. \qquad (3)$$

While the alcohol is converted into a carbonyl compound, the amine is converted into a Schiff base:

$$>NO^\cdot + H_2N{-}\dot{C}< \;\rightarrow\; >NOH + {-}N{=}C<\,. \qquad (4)$$

Reactions of types (3) and (4) have been observed in an inert atmosphere for different heterocyclic nitroxy-radicals and the nitroxy-radical (II). The interaction of heterocyclic nitroxy-radicals with the peroxy-radicals formed in the oxidation of secondary and tertiary aliphatic amines has been described.[45,46] The peroxy-radicals are destroyed via the reaction:

$$-NH{-}\overset{|}{\underset{|}{C}}OO^\cdot + >NO^\cdot \rightarrow >NOH + {-}N{=}C< + O_2\,. \qquad (5)$$

The inhibition of the oxidation reactions can be achieved not only by the addition of complete nitroxy-radicals but also as a result of the introduction into the oxidation system of primary and secondary amines, which are capable of being converted into nitroxy-radicals under these conditions.[47-49] Thus in the presence of diphenylamine the following reactions take place:

$$(C_6H_5)_2NH + RO_2^\cdot \xrightarrow{k_c} (C_6H_5)_2N^\cdot + ROOH\,; \qquad (6)$$

$$(C_6H_5)_2N^\cdot + RO_2^\cdot \xrightarrow{k_d} (C_6H_5)_2NO^\cdot + RO^\cdot\,. \qquad (7)$$

Nitroxy-radicals are usually not formed in the oxidation of tertiary amines.[47] The oxidation reactions of tertiary amines derived from indoline are an exception.[50]

In the oxidation of cumene, $k_d = 6 \times 10^3$ litre mol^{-1} s^{-1} at 57 °C [41] and $k_c = 4 \times 10^4$ litre mol^{-1} s^{-1} at 65 °C.[30] At the same temperature, $k_d > k_c$ according to Berger et al.[30] According to the data of Howard and Wiles,[51] the abstraction of a hydrogen atom from secondary aliphatic amines is much slower than the abstraction from aromatic amines.

Nitroxy-biradicals exhibit fundamentally the same inhibiting properties as the monoradicals. According to Brownlie and Ingold[52] and Ruban et al.,[53] the inhibition reaction is preceded by the decomposition of the biradical into the two corresponding monoradicals. The question of the reactivity of the nitroxy-biradicals and nitroxy-polyradicals has been discussed in detail.[2] Nitroxy-radicals can be introduced into the reaction also in an immobilised form. Thus polystyrene containing t-butylnitroxy-groups (one $>NO^\cdot$ group per 250 to 300 monomer units) is an effective inhibitor of radical reactions.[54]

Taking into account the ability of nitroxy-radicals to interact with alkyl radicals, it is to be expected that they inhibit not only oxidation reactions but also other radical processes. Indeed they behave as inhibitors of polymerisation, especially of chloroprene, acrylates and methacrylates, vinyl monomers, styrene, etc.[1,54,55]

III. KINETIC CHARACTERISTICS OF NITROXY-RADICALS AS ANTIOXIDANTS

In order to be able to discuss the kinetic parameters characterising the inhibiting capacity of nitroxy-radicals, we shall make use of the general mechanism of the oxidation processes accompanied by polymerisation in the presence of nitroxy-radicals. This scheme is based on the available published experimental data:

Scheme 1

$$RH \xrightarrow{O_2} R^\cdot\,, \qquad (0)$$

$$R^\cdot + O_2 \xrightarrow{k_1} RO_2^\cdot\,, \qquad (1)$$

$$RO_2^\cdot + RH \xrightarrow{k_2} ROOH + R^\cdot\,, \qquad (2)$$

$$ROOH \xrightarrow{k_3} RO^\cdot,\ OH,\ RO_2^\cdot\,, \qquad (3)$$

$$R^\cdot + R^\cdot \xrightarrow{k_4} \text{molecular products}\,, \qquad (4)$$

$$R^\cdot + RO_2^\cdot \xrightarrow{k_5} \text{molecular products}, \qquad (5)$$

$$RO_2^\cdot + RO_2^\cdot \xrightarrow{k_6} \text{molecular products}, \qquad (6)$$

$$R^\cdot + >NO^\cdot \xrightarrow{k_7} >NOR\,, \qquad (7)$$

$$RO_2^\cdot + >NOR \xrightarrow{k_8} ROOR + >NO^\cdot, \qquad (8)$$

$$RO_2^\cdot + >NOR \xrightarrow{k_9} \text{molecular products}, \qquad (9)$$

$$RO_2^\cdot + >NO^\cdot \xrightarrow{k_{10}} [RO_2^\cdot \cdots >NO] \text{ or } >NOH + >C{=}C< + O_2\,, \qquad (10)$$

$$>NO^\cdot + RH \xrightarrow{k_{11}} >NOH + R^\cdot\,. \qquad (11)$$

When the compound being oxidised contains C=C double bonds or when an unsaturated compound M is added to a saturated substance undergoing oxidation, the mechanism must be supplemented by the following reactions:

$$\rangle NO^{\cdot} + M^{\cdot} \xrightarrow{k_{12}} \text{molecular products,} \tag{12}$$

$$\rangle NO^{\cdot} + M \xrightarrow{k_{13}} M^{\cdot}, \tag{13}$$

$$M^{\cdot} + O_2 \xrightarrow{k_{14}} MO_2^{\cdot}, \tag{14}$$

$$MO_2^{\cdot} + M \xrightarrow{k_{15}} M^{\cdot}, \tag{15}$$

$$MO_2^{\cdot} + MO_2^{\cdot} \xrightarrow{k_{16}} \text{molecular products.} \tag{16}$$

Here R$^{\cdot}$ is an alkyl radical, $\rangle NO^{\cdot}$ the nitroxy-radical, and M the olefin molecule.

Apart from the usual reactions characteristic of the non-inhibited chain oxidation process,[56] the scheme includes stages involving the destruction of free radicals by the nitroxy-radical [reactions (7), (9), (10), and (12)] and the regeneration of the nitroxy-radicals from their reaction products [reaction (8)]. Reactions (11) and (13) refer to the initiation of free radical chains by the nitroxy-radicals as a result of their addition to the double bond or the abstraction of a hydrogen atom from the molecule of the organic substrate. All these reactions will be discussed in greater detail below.

The efficiency of nitroxy-radicals as oxidation inhibitors can be characterised very approximately by measuring the induction period. Naturally, when different nitroxy-radicals are compared, the determination must be carried out with identical amounts of the inhibitor and under the same experimental conditions. In particular, by measuring the induction periods, it has been established that nitroxy-radicals derived from quinoline and carboline are less effective inhibitors of the oxidation of polypropylene and of the oxidative degradation of polyformaldehyde than the nitroxy-radicals of type (I).[57] The antioxidant efficiencies of 15 nitroxy-radicals having different structures have been characterised[55] from the induction periods in the oxidation of polypropylene. It is of interest that the induction period in the oxidation of polypropylene[55,58] continues even after the apparent consumption of the nitroxy-radicals , i.e. after the disappearance of the corresponding EPR signal. One can therefore assume that in certain systems the nitroxy-radical behaves as an inhibitor even at very low stationary concentrations in the system—below the sensitivity limit of the EPR method.

The inhibiting capacity of nitroxy-radicals is characterised much more accurately by the rate constants for the elementary stages of the inhibition process. When alkyl radicals are destroyed by a nitroxy-radical, the rate constant k_7 or the ratio k_1/k_7 is usually determined.[25,27,51] The rate constants k_{10} for type (II) nitroxy-radicals have been measured in the oxidation of ethylbenzene and styrene. The study of the inhibited oxidation of alcohols and amines yielded the combinations of rate constants $k_{10}/k_6^{1/2}$ for nitroxy-radicals of different structure. The rate constant k_{10} refers in this instance to a disproportionation reaction of type (5) and not to the recombination of radicals.

A novel method of characterising nitroxy-radicals as inhibitors has been proposed.[59] In contrast to the traditional approach requiring the comparison of the rates of chain propagation [reaction (1)] and chain termination by the nitroxy-radical [reaction (7)] in Scheme 1, here the rates of chain termination were compared in the presence and absence of the nitroxy-radical. An expression was then obtained for the minimum concentration of the nitroxy-radical necessary for the inhibition of the oxidation of the organic compound RH:

$$[\rangle NO^{\cdot}]_{\min} > \frac{k_1 \sqrt{W_0 k_6}\,[O_2]}{k_2 k_7\,[RH]}, \tag{8}$$

where W_0 is the rate of chain initiation in reaction (0) in Scheme 1.

Table 1. Kinetic parameters of the reactions of nitroxy-radicals with organic free radicals (the designations correspond to the numbering of the reactions in Scheme 1 and to the numbering of the nitroxy-radicals—see the beginning of the review).

Source of hydrocarbon radicals	Nitroxy-radical	T, C	Value of parameter	Refs.
	k_7, litre mol^{-1} s^{-1}			
Styrene	4-Hydroxy-(I) and 4,4′-dimethoxy-(II)	50	$2.1\cdot10^4$	[53]
”	2,2′,6,6′-Tetramethyl-4,4′-dimethoxy-(II)	50	$2.8\cdot10^4$	[53]
”	2,2′4,4′-Tetramethoxy-(II)	50	$3.2\cdot10^4$	[53]
Polystyrene	4-Oxo-(I)	65	10^7	[52]
Styrene	4,4′-Diethoxy-(II)	70	$2.7\cdot10^5$	[88]
”	4,4′-Diisopropyl-(II)	60	$1.4\cdot10^5$	[89]
”	4-Hydroxy-(I)	60	$2.0\cdot10^5$	[89]
”	4,4′-Dimethoxy-(II)	60	$1.7\cdot10^5$	[89]
Methylacrylate	(I)	50	$3.0\cdot10^7$	[90]
Methyl methacrylate	(I)	50	$1.2\cdot10^7$	[90]
Ditto	3-Cyano-(V)	50	$2.0\cdot10^7$	[90]
”	4-Hydroxy-(I)	50	$8.0\cdot10^6$	[90]
Isobutyl methacrylate	(I)	50	$9.0\cdot10^6$	[90]
Methanol	4-Oxo-(I)	25*	$7.2\cdot10^8$	[28]
”	3-Carbamoyl-(V)	25	$4.6\cdot10^8$	[29]
”	(VI)	25	$3.5\cdot10^8$	[29]
Ethanol	4-Oxo-(I)	25	$6.4\cdot10^8$	[28]
”	(VI)	25	$6.2\cdot10^8$	[29]
Isopropyl alcohol	4-Oxo-(I)	25	$3.9\cdot10^8$	[28]
Ditto	(VI)	25	$3.6\cdot10^8$	[29]
Methane	3-Carbamoyl-(V)	25	$7.5\cdot10^8$	[29]
”	(VI)	25	$7.8\cdot10^8$	[29]
Cyclopentane	3-Carbamoyl-(V)	25	$3.5\cdot10^8$	[29]
”	(VI)	25	$3.6\cdot10^8$	[29]
Reaction with				
e$^-$	4-Oxo-(I)	25	$2.2\cdot10^9$	[28]
e$^-$	3-Carbamoyl-(V)	25	$9.0\cdot10^9$	[29]
e$^-$	(VI)	25	$1.9\cdot10^{10}$	[29]
H	4-Oxo-(I)	25	$5.7\cdot10^9$	[28]
H	3-Carbamoyl-(V)	25	$5.3\cdot10^9$	[29]
H	(VI)	25	$6.9\cdot10^9$	[29]
OH	4-Oxo-(I)	25	$<10^8$	[28]
OH	3-Carbamoyl-(V)	25	$3.7\cdot10^9$	[29]
OH	(VI)	25	$5.4\cdot10^9$	[29]
	k_{10}, litre mol^{-1} s^{-1}			
Ethylbenzene	4,4′-Dimethoxy-(II)	70	$1.2\cdot10^6$	[2]
”	”	60	$6.0\cdot10^5$	[25]
Cyclohexyl methyl ether	”	75	$2.4\cdot10^3$	[27]
Cumene	(II)	68	$2.5\cdot10^3$	[41]
Styrene	4,4′-Dimethoxy-(II)	65	$5.0\cdot10^4$	[52]
Cyclohexylamine	4-Hydroxy-(I)	75	$2.7\cdot10^7$	[92]
Di(n-butyl)amine	”	75	$1.5\cdot10^8$	[92]
Cyclohexanol	”	75	$2.2\cdot10^8$	[92]
Dimethylaminoethylmethacrylate	”	30—60	$10^{6.2}\exp(-2700/RT)$	[90]
Ditto	”	50	$8.2\cdot10^3$	[90]
Dimethylaminoethyl propionate	”	50	$3.0\cdot10^3$	[90]
Dimethylbutylamine	”	50	$5.6\cdot10^4$	[90]
	k_1/k_7			
Cumene	(I)	60	18	[27]
”	4-Hydroxy-(I)	60	29.5	[93]
Polypropylene	”	85	0.4	[93]
Cyclohexyl methyl ether	(I)	75	3.1	[27]
Styrene	4-Oxo-(I)	65	10	[52]
Ethylbenzene	”	60	26	[25]
n-Octane**	”	0	0.6	[94]
”	”	100	7.7	[94]
”	4-Hydroxy-(I)	100	6.2	[94]
	$k_{10}/k_6^{1/2}$, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$			
Cyclohexylamine***	(I)	75	5.4	[45]
”	(VI)	75	1.5	[45]
”	4,4′-Dimethoxy-(II)	75	18	45
Di-n-butylamine	(I)	75	21	[45]
”	(VI)	75	10	[45]
”	4,4′-Dimethoxy-(II)	75	32	[45]
Cyclohexanol	4-Hydroxy-(I)	75	125	[45]
”	(VI)	75	34	[45]
”	4,4′-dimethoxy-(II)	75	48	[45]
	k'_b, litre mol^{-1} s^{-1}			
Azobisisobutyrodinitrile	Quinone-nitrone obtained from the nitroxy-radical (III)	50	$8\cdot10^3$	[43]

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*During pulsed radiolysis.

**Radiation-chemical oxidation (^{60}Co γ-radiation).

***$E_{10}-\frac{1}{2}E_6$ = 3.0 kcal mol^{-1} at 65–85 °C.

Eqn.(8), which relates the minimum concentration of nitroxy-radicals necessary for the complete arrest of the reaction to the principal kinetic parameters of the system, can be used to determine the constant k_7 by measuring $[{>}\mathrm{NO}^{\cdot}]_{\mathrm{min}}$.

The available literature data for the kinetic parameters of the interaction of nitroxy-radicals with free radicals are presented in Table 1.

When nitroxy-radicals are used as inhibitors, one must bear in mind that they can participate in free radical formation reactions. Nitroxy-radicals are hardly involved in chain branching via interaction with the hydroperoxide formed in the oxidation process, which has been demonstrated, for example, in the study of the decomposition of propene hydroperoxide.[24] However, in the presence of certain catalysts, nitroxy-radicals can accelerate the decomposition of hydroperoxides. Thus the promoting effect of the nitroxy-radical (I) in the decomposition of tetralinyl and cyclohexyl hydroperoxides in the presence of copper-containing catalysts has been established.[60,61] The effect of nitroxy-radicals can be attributed to the formation of a complex with the catalyst. In particular, it is known that they are capable of forming complexes with univalent and bivalent copper.[62] An interesting observation has been made in the study of the kinetics of the decomposition of peroxide initiators—benzoyl peroxide[63] and dicyclohexyl peroxydicarbonate[64]—in the presence of nitroxy-radicals. It was established that, in the absence of catalysts, nitroxy-radicals are able to accelerate the decomposition of peroxide compounds, provided that the concentration of the nitroxy-radical in the system is comparable to that of the peroxide.

On the other hand, nitroxy-radicals can generate free radicals by abstracting a hydrogen atom from the molecule of the organic compound [reaction (11)] or by adding to the double bond [reaction (13) in Scheme 1]. The importance of the latter reaction also lies in the fact that nitroxy-radicals have found a practical application as inhibitors of the polymerisation of unsaturated compounds. Reaction (11) has been investigated in ethylbenzene,[65] toluene,[66] phenylhydrazones,[67] di-t-butylphenol,[68] hydrazobenzene,[69] and mercaptans.[70] Reaction (13) has been investigated only for styrene and heterocyclic nitroxy-radicals.[71-73] In the case of α-methylstyrene, where the reaction involved the participation of monoradicals, addition to the double bond was not observed even at 180 °C. However, under the same conditions, the nitroxy-biradical adds readily to α-methylstyrene. This difference between reactivities can be accounted for by the greater probability for the biradical of the adiabatic reaction pathway characterised by a low activation energy.[2] The rate constants for reactions (11) and (13) are presented in Table 2.

Taking into account the possibility of the initiation by free radicals via reaction (13) in Scheme 1, we shall estimate the optimum amounts of the nitroxy-radical necessary for the inhibition of the oxidation of hydrocarbons via Scheme (1) presented above. If the compound oxidised RH has no double bond, it is assumed that an unsaturated compound, which is a source of additional initiation, constitutes a second component of the oxidation system. An increase in the induction period with increased concentration of the nitroxy-radical has been observed experimentally, but at sufficiently high concentrations it ceases to change. This can be explained by the fact that the rate of initiation by the nitroxy-radical

Table 2. The rate constants for the reactions of nitroxy-radicals leading to the formation of free radicals.

Substrate	Nitroxy-radical	T, °C	Value of constant, litre mol^{-1} s^{-1}		Refs.
			k_{13}	k_{11}	
Ethylbenzene	4-Oxo-(I)	100—200	—	$1.2\cdot10^{3}\exp(-15\,400/RT)$	[65]
"	4,4′-Dimethoxy-(II)	100—200	—	$1.1\cdot10^{3}\exp(-14\,500/RT)$	[65]
"	4,4′-Dinitro-(II)	100—200	—	$9.6\cdot10^{8}\exp(-24\,800/RT)$	[65]
"	(II)	100—200	—	$7.8\cdot10^{5}\exp(-19\,100/RT)$	[65]
Styrene	(I)	105—120	$6\cdot10^{4}\exp(-17\,000/RT)$	—	[71]
"	4-Oxo-(I)	105	$7\cdot10^{-4}$	—	[71]
"	Biradical*	105	10^{-5}	—	[71]
α-Methylstyrene	"		$6\cdot10^{2}\exp(-15\,000/RT)$	—	[71]
Hydrazobenzene	4-Oxo-(I)	20—72**	—	$7.2\cdot10^{2}\exp(-5\,000/RT)$	[69]
"	(I)	20—72	—	$4.1\cdot10^{2}\exp(-5\,000/RT)$	[69]
"	4-Hydroxy-4-ethyl-(I)	20—72	—	$2.3\cdot10^{2}\exp(-5\,000/RT)$	[69]
"	3-Formyl-(V)	20—72	—	$58\exp(5\,000/RT)$	[69]
Styrene	4-Benzoyl-(I)	60	$3.7\cdot10^{-6}$	—	[72]
"	(I)	80	10^{-5}; $2.2\cdot10^{-5}$***	—	[73]
4-Methyl-2,6-di-t-butyl-methylenequinone	4-Hydroxy-(I)	20—60	$1.6\cdot10^{2}\exp(-29\,000/RT)$	—	[95]
Raw rubber	(I)	90—130	—	$10^{8}\exp(-18\,000/RT)$	[80]
Non-1-ene	4-Benzoyl-(I)	120	$<10^{-5}$	—	[91]
β-Carotene	(I)	50	$4.0\cdot10^{-4}$	—	[33]
Cetane	4-Oxo-(I)	190—220	—	$5.2\cdot10^{10}\exp(-36\,000/RT)$	[96]
"	(III)	160—194	—	$1.7\cdot10^{5}\exp(-23\,000/RT)$	[96]
Silane****	4-Oxo-(I)	150—182	—	$6.0\cdot10^{11}\exp(-34\,000/RT)$	[96]
"	(III)	110—145	—	$9.6\cdot10^{6}\exp(-21\,500/RT)$	[96]
"	4,4′-Dimethoxy-(II)	85—115	—	$4.5\cdot10^{8}\exp(-23\,500/RT)$	[96]

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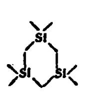
*The biradical $ROOC(CH_2)_4COOR$, where R is the radical residue from the nitroxy-radical (I).

**The activation energies are almost identical for all the nitroxy-radicals.

***At a pressure of 2000 atm.

****The silane is



becomes higher than the rate of thermal initiation. The induction period is given by

$$\tau=\frac{p}{k_2}\cdot\frac{k_7\left[>\mathrm{NO}^{\cdot}\right]}{W_0+k_{13}\left[>\mathrm{NO}^{\cdot}\right][\mathrm{M}]}\ ,$$

where p is the fraction of the substrate which has reacted at the instant when the induction period ends. At the nitroxy-radical concentration corresponding to the start of the region of constant τ, we have

$$k_{13}\left[>\mathrm{NO}^{\cdot}\right][\mathrm{M}]\gg W_0\ ;$$

whence

$$\tau=\frac{pk_7}{k_2k_{13}[\mathrm{M}]}\ . \qquad (9)$$

The rate of the oxidation process is then given by

$$W=k_2k_{13}[\mathrm{RH}][\mathrm{M}]/k_7$$

Eqn.(9) describes the region where the induction period is independent of the concentration of the nitroxy-radical. The optimum concentration of the nitroxy-radical, corresponding to the region of the independence of the induction period, is

$$\left[>\mathrm{NO}^{\cdot}\right]_{\mathrm{opt}}=W_0/k_{13}[\mathrm{M}]\ .$$

An increase in the concentration of the nitroxy-radical above $[>\mathrm{NO}^{\cdot}]_{\mathrm{opt}}$ is undesirable, since it does not lead to a further increase of the induction period. Calculation of the quantity $[>\mathrm{NO}^{\cdot}]_{\mathrm{opt}}$ may be of practical value when nitroxy-radicals are used for the antioxidant stabilisation of materials containing double bonds. The parameter characterising the inhibiting efficiency of nitroxy-radicals under the conditions of significant additional initiation can be deduced from Eqn.(9):

$$K=k_7/k_2k_{13}$$

IV. THE INHIBITION COEFFICIENT AND REGENERATION OF NITROXY-RADICALS

One of the most important characteristics of the inhibitors of radical processes, including nitroxy-radicals, is the stoichiometric inhibition coefficient f. The integral definition, according to which f is equal to the number of free radicals destroyed by one inhibitor molecule, is widely used in the chemical literature:

$$f\cdot[\mathrm{InH}]_0=W_0\tau\ ,$$

where $[\mathrm{InH}]_0$ is the initial inhibitor concentration. A method of determining f in the case of weak inhibitors which do not give rise to a distinct induction period has been described.[39]

However, in the integral definition no account is taken of the fact that f depends on the ratio of the rates of the individual elementary stages of the inhibition process. The role of this ratio is evident from the following simple example. In a system containing the free radicals $\mathrm{R}^{\cdot}$ to which the inhibitor InH has been introduced, two radical destruction reactions can take place:

$$\mathrm{R}^{\cdot}+\mathrm{InH}\rightarrow\mathrm{RH}+\mathrm{In}^{\cdot}\ , \qquad (10)$$

$$\mathrm{R}^{\cdot}+\mathrm{In}^{\cdot}\rightarrow\mathrm{RIn}\ . \qquad (11)$$

Even in this case the quantity f depends on the ratio of the rates of reactions (10) and (11). If the rate of reaction (11) greatly exceeds that of reaction (10), then $f = 2$. In the opposite case $f = 1$ and for comparable rates of the two reactions we have $1 < f < 2$.

A differential, i.e. "rate" treatment of the quantities f for the reactions involving inhibition by nitroxy-radicals has been described.[59] In this case the expression for f represents the ratio of the sum of the rates of the elementary stages in which the chain propagating free radicals are destroyed to the sum of the rates of the elementary stages in which the inhibitor is consumed. According to Scheme 1,

$$f=\frac{1+\beta\left[>\mathrm{NOR}\right]/\left[>\mathrm{NO}^{\cdot}\right]}{1-\{k_8/(k_8+k_9)\}\cdot\beta\cdot\left[>\mathrm{NOR}\right]/\left[>\mathrm{NO}^{\cdot}\right]}\ , \qquad (12)$$

where

$$\beta=\frac{(k_8+k_9)[\mathrm{RO}_2^{\cdot}]}{k_7[\mathrm{R}^{\cdot}]}=\frac{(k_8+k_9)k_1[\mathrm{O}_2]}{k_2k_7[\mathrm{RH}]}\ .$$

The rate of change of the concentration of $>\mathrm{NOR}$—the product of the reaction of the initial nitroxy-radical—in the course of the oxidation process is described by the expression

$$\mathrm{d}\left[>\mathrm{NOR}\right]/\mathrm{d}t=k_7[\mathrm{R}^{\cdot}]\left[>\mathrm{NO}^{\cdot}\right]-(k_8+k_9)[\mathrm{RO}_2^{\cdot}]\left[>\mathrm{NOR}\right]\ .$$

The rearrangement of this equation and integration using the approximation $[\mathrm{RO}_2^{\cdot}] = [\overline{\mathrm{RO}_2^{\cdot}}]$, i.e. for the average concentration of the radicals $\mathrm{RO}_2^{\cdot}$ in the course of the entire process, lead to the expression

$$\frac{\left[>\mathrm{NOR}\right]}{\left[>\mathrm{NO}^{\cdot}\right]}=\frac{1}{\beta}(1-\mathrm{e}^{-2t/t_c})\ . \qquad (13)$$

The time during which the rates of formation and consumption of the product $>\mathrm{NOR}$ become equal is

$$t_c=2/(k_8+k_9)[\overline{\mathrm{RO}_2^{\cdot}}]=2(\beta W_0)^{-1}\left[>\overline{\mathrm{NO}^{\cdot}}\right]\ .$$

Comparison of Eqns.(13) and (12) shows that, when $t = t_c$, the ratio $[>\mathrm{NOR}]/[>\mathrm{NO}^{\cdot}]$ is close to $1/\beta$. During the reaction, the quantity f changes from 1 at the beginning of the oxidation to $2[1 + (k_8/k_9)]$. Estimation of the parameters β and t_c using the known rate constant k_7, k_{14},[48] k_8,[24,32] and k_{15}[74] leads to $\beta = 10^{-3}$–10^{-2} and $t_c = 10^4$–10^5 s. For short reaction times (up to 3–4 h), the condition $t = t_c$ is not attained and f continuously increases during the reaction without reaching, however, its maximum value.

According to Vardanyan et al.,[75] the inhibition coefficient in oxidation inhibited by amines is defined by the equation

$$f=2(k_8+k_9)/k_9\ . \qquad (14)$$

This expression is a special case of Eqn.(12) and is valid for systems where $k_8 \gg k_7$, i.e. the time required for the attainment of a stationary concentration of the inhibitor reaction product is much shorter than the duration of the oxidation reaction. In studies of the oxidation of polypropylene,[26,76] it has been stated that f increases with increase of oxygen concentration in the system. Indeed an increase in the O_2 concentration increases the efficiency of the inhibition by the nitroxy-radical as a result of the decrease of t_c. On the other hand, the maximum value of f, defined by Eqn.(14), is independent of the oxygen concentration.

The high absolute values of f under conditions where nitroxy-radicals are used in oxidation processes are caused by the inhibitor regeneration reaction [reaction (8) in Scheme (1)] and the increase of f during the process is associated with the increase of its rate as the primary product of the interaction of the nitroxy-radical with the alkyl radical $\mathrm{R}^{\cdot}$ accumulates. The increase of f naturally leads to a decrease of the apparent rate of consumption of the nitroxy-radical during the oxidation process. The inhibition coefficients in different systems are listed in Table 3.

Table 3. The inhibition coefficients (f) of nitroxy-radicals.

Nitroxy-radical	Substrate oxidised	f	Refs.
p-Ethoxy-(II)	Liquid paraffin	28	[39]
4,4′-Dinitro-(II)	Ditto	15	[39]
(I)	"	510	[39]
4-Oxo-(I)	"	410	[39]
Di-t-butylnitroxy-radical	"	225	[39]
4-Benzoyl-(I)	"	630	[39]
"	n-Hexylbenzene	3900	[30]
"	ββ-Dideuterio-n-hexylbenzene	1100	[30]
(I)	Liquid paraffin + 10 wt.% of diphenylmethane	190	[30]
(I)	Liquid paraffin + 10 wt.% of 1,1-diphenylethane	580	[30]
4-Oxo-(I)	n-Hexylbenzene	720	[30]
(I)	Cyclohexa-1,3-diene	90	[77]
4-Oxo-(I)	Tri-n-butylamine	40	[46]
4-Hydroxy-(I)	Benzaldehyde	100	[78]
"	Acetaldehyde + styrene	20	[59]

In particular, it follows from Table 3, that in the oxidation of higher paraffins, f = 15–35 for aromatic nitroxy-radicals, 225 for the aliphatic t-butylnitroxy-radical, and 500–600 for heterocyclic nitroxy-radicals. The observed difference between the values of f is apparently associated with the fact that aromatic nitroxy-radicals readily enter into side reactions, which lead to their irreversible consumption [reaction (1)].

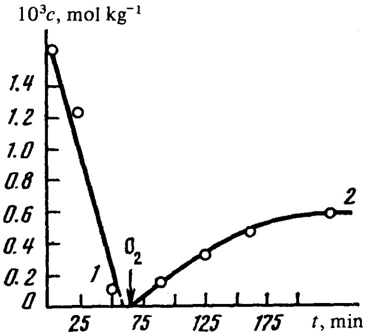


Figure 3. Kinetic curves for the consumption of the 4-hydroxy-derivatives of the nitroxy-radical (I) in an atmosphere of argon (curve *1*) and for the accumulation of the nitroxy-radical after the admission of oxygen (curve *2*) in isotactic polypropylene at 114 °C.[27]

The idea that the regeneration reaction (8) is in fact responsible for the high values of f is nowadays generally accepted. The occurrence of this reaction is convincingly indicated by the available experimental data. In an inert atmosphere, nitroxy-radicals interact with organic free radicals generated in the system, which results in the complete consumption of the nitroxy-radicals. When oxygen is passed subsequently through the reaction mixture, nitroxy-radicals reappear and their concentration increases to a stationary value (Fig.3). In particular, such regeneration has been observed in the interaction of nitroxy-radicals and nitroxy-biradicals with the products of the radiation-chemical reactions of n-octane[35] and the photochemical reactions of rubber[79] and also in the decomposition of the initiator AIBN in polypropylene,[76] aliphatic alcohols, and amines.[45]

A detailed study has been made of the kinetics of certain reactions which can, in principle, lead to the generation of nitroxy-radicals.[27] Apart from the primary reaction (8) in Scheme 1 already mentioned, the following reactions were also investigated:

$$\rangle NOR \xrightarrow{k_e} R^{\cdot} + \rangle NO^{\cdot}, \qquad (15)$$

$$\rangle NOR + O_2 \xrightarrow{k_f} \rangle NO^{\cdot} + \text{products}. \qquad (16)$$

The rate constants for different regeneration reactions are listed in Table 4. The data presented confirm the conclusion that reaction (8) is the main process responsible for the regeneration of nitroxy-radicals from their reaction products.

Table 4. The rate constants for the regeneration of nitroxy-radicals from hydroxylamine ethers.

Ether $\rangle$NOR	T, °C	Value of parameter	Refs.
		k_e, s	
O-1,1-Diphenylethyl-4-oxo-(I)	20—50	$10^{14.8}\exp(-24\,500/RT)$	[37]
"	50	$1.6 \cdot 10^{-3}$	[37]
O-Methyl-(I)	100	10^{-7}	[27]
O-Cyclohexyl-(I)	100	10^{-7}	[27]
O-t-butyl-(I)	100	$1.5 \cdot 10^{-5}$	[27]
O-Dimethylcyanomethyl-(I)	65—87	$10^{12.6}\exp(-25\,000/RT)$	[27]
"	100	$1.6 \cdot 10^{-2}$*	—
NNO-Tri-t-butylhydroxylamine	60—100	$1.2 \cdot 10^{9}\exp(-22\,900/RT)$	[30]
"	100	$5.8 \cdot 10^{-5}$	[30]
		k_f, litre mol^{-1} s^{-1}	
O-t-butyl-(I)	110	$5.0 \cdot 10^{-4}$	[27]
O-methyl-(I)	110	$5.0 \cdot 10^{-4}$	[27]
		k_8, litre mol^{-1} s^{-1}	
Bi-[*O*-cyclohexyl-(I)] (from the biradical)	100	$3.0 \cdot 10^{3}$**	[35]
O-Phenyl-(I)	65	1.0***	[27]
O-Ethyl-(I)	65	8.0***	[27]
O-Cyclohexyl-(I)	65	26.0***	[27]
O-t-Butyl-(I)	65	4.0***	[27]
NNO-tri-t-butylhdyroxylamine	100	44****	[30]

---

*Obtained by extrapolation.

**$RO_2^{\cdot} = n\text{-}C_8H_{17}OO^{\cdot}$.

***$RO_2^{\cdot} = (CH_3)_2CNOO$.

****$RO_2^{\cdot} = (CH_3)_2CHC_6H_4\text{-}p\text{-}C(CH_3)_2\text{-}OO^{\cdot}$.

The regeneration of nitroxy-radicals can apparently proceed not only with participation of the peroxy-radicals $RO_2^{\cdot}$ but also in the interaction with the oxy-radicals $RO^{\cdot}$. However in real oxidation systems the $RO_2^{\cdot}$ concentration usually exceeds by two orders of magnitude the $RO^{\cdot}$ concentration, as a result of which the main regenerating agent is in fact the peroxy-radical. In the styrene–acetaldehyde binary system, the type (I) nitroxy-radical is consumed at the same rate as in the oxidation of styrene alone,[59] which shows that the regeneration is effected by the peroxy-radicals derived from styrene, whose concentration is much higher than the concentration of acetyl peroxy-radicals. According to Vardanyan and Denisov,[77] the radicals $HO_2^{\cdot}$ are also capable of regenerating nitroxy-radicals.

It has been suggested[48] that the regeneration is caused by the hydroperoxide:

$$\mathrm{ROOH} + {>}\mathrm{NOH} \rightarrow \mathrm{RO}^{\bullet} + {>}\mathrm{NO}^{\bullet} + \mathrm{H_2O}\ .$$

However, the available experimental data do not allow one to rule out the possibility that the nitroxy-radical is regenerated by the free radicals which can be formed from the hydroperoxide. The regeneration of nitroxy-radicals in an inert atmosphere under the influence of polymers subjected to prior oxidation has been investigated.[26] The oxidised polymer contains hydroperoxy-groups, which the authors[26] believe decompose with formation of the radicals $\mathrm{RO}^{\bullet}$ responsible for the regeneration of the nitroxy-radical.

The peroxy-radicals $\mathrm{RO}_2^{\bullet}$ are capable of regenerating the nitroxy-radical not only from the ethers but also from the hydroxylamine itself:[80]

$${>}\mathrm{NOH} + \mathrm{RO}_2^{\bullet} \rightarrow {>}\mathrm{NO}^{\bullet} + \mathrm{ROOH}\ .$$

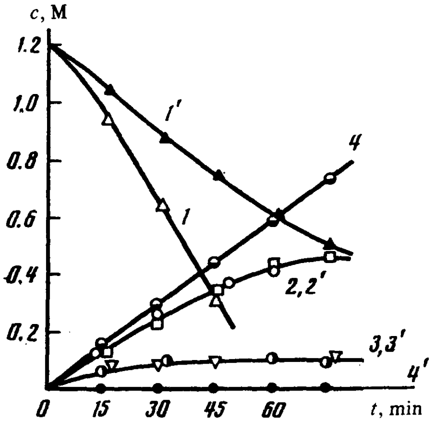


Figure 4. Kinetic curves for the consumption of styrene (curve *1*) and the accumulation of benzaldehyde (curve *2*), styrene oxide (curve *3*), and a polymeric product (curve *4*) in the coupled oxidation of styrene and acetaldehyde by air in benzene (70 °C, 50 atm); the primed numbers designate the corresponding curves in the presence of 2.2×10^{-3} M 4-hydroxy-derivative of the nitroxy-radical (I).[59]

The formation of hydroxylamines and the above regeneration mechanism have been observed mainly for chain termination resulting from the interaction with nitroxy-radicals having labile hydrogen atoms (for example, in the oxidation of alcohols or amines). In this cast too, the regeneration by the radicals $\mathrm{RO}_2^{\bullet}$ takes place at a higher rate than in the interaction with O_2 or with the hydroperoxide. It is noteworthy that the rate of regeneration of the nitroxy-radical from hydroxylamines is higher than from their ethers. The regeneration of nitroxy-radicals from hydroxylamine ethers as a result of the abstraction of a hydrogen atom in the β-position is also possible:

$$\mathrm{R^1CH_2CH_2ON}{<} + \mathrm{RO}_2^{\bullet} \rightarrow {>}\mathrm{NO}^{\bullet} + \mathrm{R^1CH{=}CH_2} + \mathrm{ROOH}\ .$$

The regeneration phenomenon must also be taken into account in those cases where the nitroxy-radicals are used to determine the rate of chain initiation W_0. In order to obtain the true values of W_0, it is essential to have accurate information about the inhibition coefficient in each specific case. On the other hand, the measurement of the rate of consumption of nitroxy-radicals in an inert atmosphere constitutes an extremely convenient method for the study of the kinetics of the decomposition of radical process initiators,[41,44,76] in particular the study of solvent cage effects in the decomposition process.[81] Nitroxy-radicals can be used as radical counters, for example in radiolytic processes[82] and in the determination of sulphur-containing radicals.[83]

In a study[84] of the oxidation of β-carotene (a polyunsaturated hydrocarbon) in the presence of the nitroxy-radical (III), it was shown that the observed high inhibition coefficients are related to an unusual type of regeneration—a relay process. In this instance, the regeneration effect is due to the "relay" radical reaction of the nitroxy-radical and its reaction products, which interact alternately with peroxy- and alkyl radicals derived from the substrate. An essential condition for such relay chain termination by the nitroxy-radical is a definite ratio of the concentrations of the alkyl and peroxy-radicals in the system:

$$10^{-3} - 10^{-2} \leqslant [\mathrm{R}^{\bullet}]/[\mathrm{RO}_2^{\bullet}] \leqslant 10^{-1}\ .$$

However, one should note that the nitroxy-radicals cannot evidently be regenerated in all cases from the reaction products. This is indicated by the finding that $f = 1$ is observed also for nitroxy-radicals in a number of instances, for example, in the oxidation of cumene.[41]

V. CHEMICAL REGULATION OF OXIDATION PROCESSES WITH THE AID OF NITROXY-RADICALS

In our investigations under the supervision of Emanuel' and with participation of Blyumberg and Tavadyan, it was established that nitroxy-radicals can be used to regulate the composition of the products in the oxidation of organic compounds. This possibility is associated with the phenomenon of the selective inhibition of many-centre chain processes, first described by Maslov and co-workers.[85,86] When the nitroxy-radical (I) was introduced into the coupled oxidation reaction of acetaldehyde and styrene[85] or of acetaldehyde and allyl chloride,[86] an appreciable increase in selectivity of the formation of monomeric oxygen-containing products was observed. In the absence of the nitroxy-radical, most of the initial unsaturated compound was converted into a polymeric product. Thus, in the case of styrene, an increase of selectivity with respect to monomeric products from 50 to 95 mole % and in the case of allyl chloride from 35 to 70 mole % was achieved.

The acetaldehyde—styrene binary oxidation system was selected for the detailed investigation of the mechanism of the selective inhibition by nitroxy-radicals. The conditions for selective inhibition, which will be briefly discussed below, were selected in relation to this system.[59] The kinetic curves for the coupled oxidation of styrene and acetaldehyde are illustrated in Fig.4. Examination of the experimental data permits the conclusion that in the system investigated there are two reaction chain carriers—the acetylperoxy-radicals $\mathrm{RCOOO}^{\bullet}$ and the polyperoxy-radicals $\mathrm{MO}_2^{\bullet}$ (M = styrene molecules), which propagate two independent process pathways—monomeric and polymeric respectively. This claim is supported in particular by the absence of dependence of the rate of accumulation of the monomeric products on the presence of nitroxy-radicals in the system. The existence of a definite nitroxy-radical concentration at which the radicals do not inhibit the oxidation of the aldehyde but fully inhibit the formation of polymeric products, indicates the independence of the concentration of the radicals RCOOO$^{\cdot}$ or the concentration of the radicals $MO_2^{\cdot}$, i.e. a negligibly low rate of the radical "exchange" reaction

$$MO_2^{\cdot} + RCHO \xrightarrow{O_2} RCOOO^{\cdot} + MOOH \ .$$

In this case the addition of the radicals RCOOO$^{\cdot}$ to the double bond of the monomer is in essence a reaction involving the destruction of the chain in the monomeric reaction pathway:

$$RCOOO^{\cdot} + M \xrightarrow{k_g} M^{\cdot} \qquad (17)$$

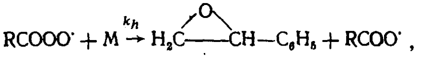
Taking into account the simultaneous occurrence in the system of two independent processes, one may conclude that, as a result of reaction (12) (see Scheme 1), the nitroxy-radical reduces the concentration of the radicals $MO_2^{\cdot}$ without affecting the stationary concentration of RCOOO$^{\cdot}$. The appreciable change in the ratio of the concentrations of the radicals propagating different process pathways in favour of RCOOO$^{\cdot}$ leads to the observed increase of the selectivity of the reaction with respect to monomeric products.

The presence of the induction period caused by the introduction of the nitroxy-radical indicates the fulfillment of the condition $W_7 \gg W_{17}$: on the other hand, at the end of the induction period $W_{17} > W_7$. The rate of reaction (12) should then exceed the rate of reaction (16) (in Scheme 1), which is a condition for the inhibition of the polymeric process pathway, i.e.

$$k_7[\mathrm{RCO}^{\cdot}]\left[\rangle \mathrm{NO}^{\cdot}\right] < k_g\,[\mathrm{RCOOO}^{\cdot}]\,[M]\ ,$$

$$k_{12}\,[\mathrm{M}^{\cdot}]\left[\rangle \mathrm{NO}^{\cdot}\right] > k_{16}\,[\mathrm{MO}_2^{\cdot}]^2 \quad .$$

Bearing in mind that, during the occurrence of the chain propagation reactions



$$\mathrm{RCOOO}^{\cdot} + \mathrm{M} \xrightarrow{k_h} \mathrm{H_2C}\overset{\mathrm{O}}{\overline{\quad}}\mathrm{CH{-}C_6H_5} + \mathrm{RCOO}^{\cdot}\ , \qquad (18)$$

$$\mathrm{RCOOO}^{\cdot} + \mathrm{M} \xrightarrow{k_i} \mathrm{C_6H_5CHO} + \mathrm{RCOO}^{\cdot} + \mathrm{HCHO}\ , \qquad (19)$$

we have

$$\frac{[\mathrm{RCOOO}^{\cdot}]}{[\mathrm{RCO}^{\cdot}]} = \frac{k_1\,[\mathrm{O_2}]}{(k_h + k_i)[\mathrm{M}]};\ \frac{[\mathrm{MO}_2^{\cdot}]}{[\mathrm{M}^{\cdot}]} = \frac{k_{14}\,[\mathrm{O_2}]}{k_{15}\,[\mathrm{M}]}\ ,$$

$$k_g\,[\mathrm{RCOOO}^{\cdot}]\,[\mathrm{M}] = k_{12}\,[\mathrm{M}^{\cdot}]\left[\rangle \mathrm{NO}^{\cdot}\right] = W_0\ ,$$

the following equation is obtained:

$$\frac{k_1 k_g[\mathrm{O_2}]}{k_7(k_h + k_i)} > \left[\rangle \mathrm{NO}^{\cdot}\right] > \frac{k_{14}\,(W_0 k_{16})^{1/2}\,[\mathrm{O_2}]}{k_{12}k_{15}\,[\mathrm{M}]}\ . \qquad (20)$$

Condition (20) defines the limits of the nitroxy-radical concentration range in which selective inhibition of polymerisation processes, accompanying the oxidation in the acetaldehyde–styrene system, should be observed. The boundary condition for other systems can be derived analogously.

The phenomenon of selective inhibition can be observed in the oxidation of not only binary systems but also of individual compounds having several functional groups with different reactivities, for example, unsaturated aldehydes. This has been used, in particular, in the development of an effective method for the preparation of methacrylic acid[87] by the liquid-phase catalytic oxidation of methacrolein in the presence of the nitroxy-radicals (I) or their 4-hydroxy-derivatives. It is distinguished by simplicity and economy compared with the industrial method of synthesis of methacrolein from acetone via the cyanohydrin. Fig.5 illustrates kinetic curves for the liquid-phase oxidation of methacrolein to methacrylic acid. The use of nitroxy-radicals makes it possible to increase the selectivity in the formation of methacrylic acid to 75–80 mole %. Acetic acid, which also has many applications, is mainly formed as a side product.[97]

In conclusion we shall formulate the necessary and sufficient conditions for selective inhibition:

(1) the existence in the system of two types of free radicals each of which is responsible for the formation of a specific product or group of products; (2) the independence of the concentration of radicals of one type from that of the radicals of the other type; (3) the presence in the system of a definite amount of inhibitor satisfying condition (20); (4) the maintenance of the required inhibitor concentration for a period sufficiently long to ensure the occurrence of a chemical reaction; when nitroxy-radicals are used, this condition is usually fulfilled by means of effective regeneration.

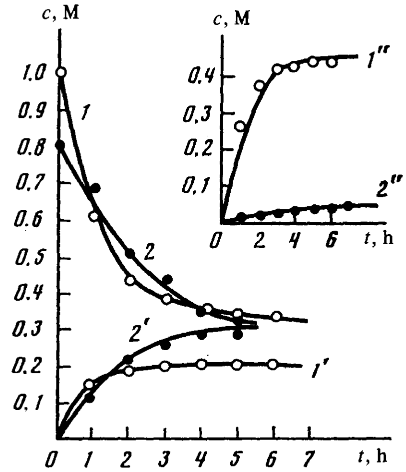


Figure 5. Kinetic curves for the consumption of methacrolein (curves *1* and *2*) and the accumulation of methacrylic acid (curves *1'* and *2'*) and the sums of the side products (curves *1''* and *2''*) in the liquid-phase oxidation of methacrolein by air in benzene (70 °C, 25 atm, 2.5 g litre^{-1} of the TiB_2 catalyst: 1) without inhibitor; 2) in the presence of 1.2×10^{-5} M 4-hydroxy-derivative of the nitroxy-radical (I).[97]

The possibilities in the application of nitroxy-radicals in chemistry are not limited to those already known, the most important of which at the present time are the photostabilisation and inhibition of the oxidative degradation of polymers, the stabilisation of monomers, and also the detection and determination of the active chemical species. Under conditions where the petrochemical raw material resources are diminishing, the ability of nitroxy-radicals to increase the selectivity of the oxidative conversion of hydrocarbons into the required products is very important from both theoretical and practical points of view. The possibility of increasing the efficiency of such processes is associated with the search for new, more effective and at the same time cheap nitroxy-radicals and also with the development of economical methods of synthesis of nitroxy-radicals which are likely to satisfy the future requirements of the chemical industry.

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Compounds of the Halogen Cations

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The conditions for the synthesis, the thermodynamics of the formation and decomposition, the structure, and the nature of the chemical bond in the halogen cations are examined. The electronic, vibrational, nuclear quadrupole resonance, and nuclear magnetic resonance spectra are analysed and questions concerning the practical application of the halogen cations as some of the most powerful oxidants, are discussed.
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I. INTRODUCTION

The compounds of halogen cations are complexes with a singly charged cation $[Hal(Hal'_nHal''_m)]^+$, where Hal is the complex forming halogen (Cl, Br, I, or At) in the +3, +5, or +7 oxidation states, while Hal' and Hal" are halogen ligands (ranging from F to At). The ligands can also be numerous interhalogen compounds and apparently pseudohalogens. Fluorine is the commonest ligand.

The term "halogen cations" was introduced by Arotsky and Symons[1] and has come to be widely used.[2-5] The first review of the chemistry of the halogen cations was published in 1962[1] and was followed by others.[4,6-9] During the period since the publication of the last review, the number of studies on the chemistry of the halogen cations has doubled and it became necessary to give a systematic account of the accumulated data and to describe more fully the studies by Soviet workers.

There is now no doubt that the complex forming agent in the cation $[Hal(Hal'_nHal''_m)]^+$ is always the most electropositive of the halogens. With increase of its electropositivity and also with increase of the strength of the Lewis acids from which the anions have been derived ($BF_3 < PF_5 < PtF_5 < SbF_5 < AsF_5$). the stability of the halogen cation compounds increases. The compounds of halogen cations are mainly ionic species with a certain amount of covalent character in the chemical bonds, which is manifested by the formation of halide bridge bonds between the cation and the anion. Extremely electrophilic cations, namely $[I_3]^+$, $[ICl_2]^+$, $[IF_6]^+$, $[ClF_2]^+$, etc., can exist only in media with very weak basic properties (superacids, SO_2, SbF_5, IF_5, etc). With weakly basic anions, such as $[SbF_6]^-$, $[AlCl_4]^-$, $[SbCl_6]^-$, etc., cations of this kind form crystalline phases.

The synthesis of the halogen cation compounds is based on the interaction of interhalogen compounds, halogens, or their mixtures with strong Lewis acids (acceptors of halogen atoms), for example in accordance with the mechanism

$$BrF_3+AsF_5=[BrF_2][AsF_6] \ .$$

On the other hand, if a strong Lewis base (a halogen atom donor) is introduced into the reaction instead of the Lewis acid, then representatives of another group of complexes, namely compounds of halogenate anions,[10-12] are formed from the solution, for example:

$$BrF_3+CsF=Cs[BrF_4] \ .$$

For this reason in solutions of interhalogen compounds, compounds of halogen cations and the halogenate anions interact as Lewis acids and bases:[6,13,14]

$$[BrF_2][AuF_4]+Ag[BrF_4]=Ag[AuF_4]+2BrF_3 \ .$$

The chemistry of the halogen cation compounds is so far in the initial stage of its development. In this review, which is the first in the Soviet literature, an attempt is made to identify the most promising research trends and to describe the principal properties and reactions of the halogen cation compounds and the methods of their synthesis.

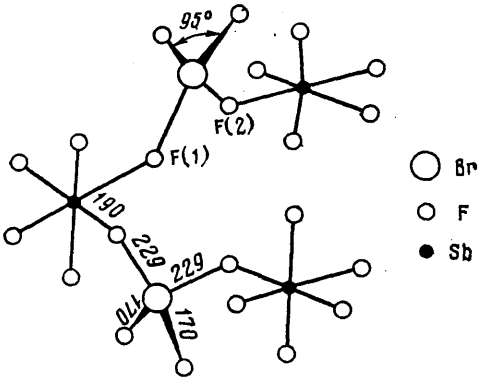

Figure 1. Schematic illustration of the structure of $[BrF_2]$. $.[SbF_6]$ [17,18] (the interatomic distances are indicated in pm).

II. THE STRUCTURE AND NATURE OF THE CHEMICAL BOND

All the triatomic halogen cations, namely $[I(I)_2]^+$, $[BrF_2]^+$, $[ClF_2]^+$, and similar species, have a bent structure (Fig.1), in which the angle between the bonds is 91–103° (C_{2v} symmetry).[15-21] We may note that the triatomic halogenate anions, i.e. $[I_3]^-$, $[BrF_2]^-$, $[ICl_2]^-$, etc, are linear and symmetrical.[10] With increase of the electronegativity of the central atom, its effective positive charge diminishes $\{\delta = 1.48$ for $[BrF_2]^+$ and 0.98 for $[ClF_2]^+\}$ and at the same time the effective charge of the ligands changes (from $\delta = -0.24$ to $\delta = 0.01$ for the same cations).[16,22-27] The effective charges on the central atom and the ligands in the cation $[Cl(ClF)]^+$ are respectively 0.324 and 0.338.[23-29] The values of δ quoted in the literature differ and depend on the methods of calculation. In particular, δ for Hal = I in the $[I_3]^+$ cation varies over the range 0.55–0.79.[15,30,31]

As in the triatomic halogenate anions, in the triatomic halogen cations only the *p* orbitals of the central atom and the ligands participate in the formation of the bond.[32] The population of the *d* orbitals in the $[I_3]^+$ and $[I_3]^-$ ions is insignificant and their involvement in bond formation is not obligatory. When an electron pair is removed from the $[I_3]^-$ anion with formation of the $[I_3]^+$ cation, the valence state of the central atom remains unchanged and only the degree of its oxidation increases.[32] An increase in the overall *f*-electron density on the complex-forming agent (iodine) compared with the free I^- ion has been noted but the complex-forming agent–ligand interatomic distance in the $[I_3]^+$ ion is the same as in gaseous iodine.

Under certain conditions, iodine atoms can produce the diamagnetic cation $[I_4]^{2+}$, which has no complex-forming agent[34-36] and the chain cations $[I_{15}]^{3+}$ (Fig.2). The latter cation consists of three $[I_5]^+$ ions linked to one another with the central atoms E(1), I(1), and E(2). The bond lengths in the ligands and in the gaseous iodine molecule are comparable, the smallest distance between the iodine atoms in neighbouring chains being 390.6 pm.[37] According to Chung and Cady,[38] the existence of the cation $[I_7]^+$ is doubtful.

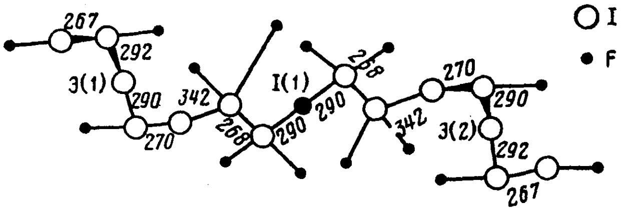

Figure 2. The configuration of the ion $[I_{15}]^{3+}$ [37] (the interatomic distances are given in pm): E(1), E(2), and I(1) are central atoms.

The angular structure of the cations $[ClF_2]^+$ and $[BrF_2]^+$ (Fig.1) corresponds best to the model comprising localised *p* orbitals with two covalent p_σ bonds.[16,22-26,39] The ligands of the cations together with the *cis*-bridging halogen atoms of the anion [F(1) and F(2), see Fig.1] form a deformed square. The sterically active unshared electron pairs of the complex-forming agent are in the *trans*-positions above and below the plane of the square (Fig.3*b*) and the cations are therefore classified as pseudohexacoordinated.[15,20,26,27] If the cation is regarded as a planar square, then the chemical bonds can be represented by two mutually perpendicular asymmetric four-electron semi-ionic p_σ bonds formed by the np_x and np_y orbitals of the central atom. The involvement of the *nd* orbitals is in this case insignificant and they are regarded[23,40] merely as having polarisation functions. For example, the population of the 3*d* orbital of the chlorine atom in the cation $[ClF_2]^+$ is only 0.05e.[40]

Fig.3 presents models of the valence bonds in the triatomic cations. When E = Cl or Br and X = Y = F, the interatomic X–X, Y–Y, and X–Y distances are 340, 230–250, and 270–280 pm respectively.[16] The E–X bond length increases, for the same complex-forming agent, on passing from X = Cl to X = I.[17,41] The E–Y bond order is 0.42–0.47.[42] The bond length ratio (E–X)/(E–Y) in the cations considered is 1.04–1.05 and diminishes with increase of the E–Y bond strength on passing from E = Cl to E = I.[8]

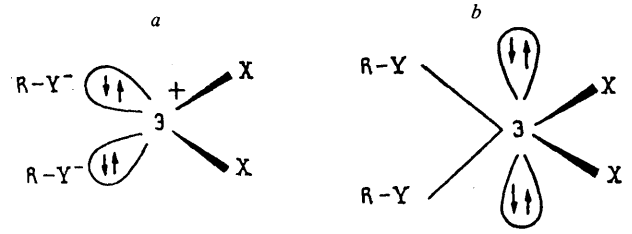

Figure 3. The planar ionic (*a*) and bridged (*b*) structures of the halogen cation compounds with an angular cation;[15,26] E = complex forming agent, X = ligands, and Y = bridging ligands of the anions.

With decrease of the bond angle in the cation, the degree of covalence of the bond between the complex-forming agent and the bridging ligand increases.[26] If the bridging ligands of the anions form strong bonds with the complex-forming agent in the cation, then all the electron pairs occupy octahedral sites with the angle between the bonds approximately 90°.[39,43] It is believed[27] that the strength of the covalent bond between the cation $[BrF_2]^+$ (Fig.1) and the anions increases from $[SbF_6]^-$ to $[GeF_6]^- \cong [Sb_2F_{11}]^-$.[23-25,27] Owing to the strong solvation of $[BrF_2]^+$ in liquid BrF_3, the Br–F bond length increases, which induces a shift of the ν_1 band in the Raman spectrum from 705–707 cm^{-1} to 625 cm^{-1}.[44] In the crystals of $[ICl_2][SbCl_6]$, the iodine atoms of the two ligands of the cation and the two bridging ligands are disposed virtually in the same plane, as in the structure of the anion $[ICl_4]^-$.[19,30,45]

The interhalogen compounds $[I(ICl)_2]^+$ (Fig.4)[46-48] and $[I(IBr)]^+$[48] can also serve as ligands in the cations. In the coordinated ICl and IBr molecules the bonds are shorter than in the single molecules. The anion $[SbCl_6]^-$ converts the cation $[I(ICl)]^+$ into a symmetrical ion, while the anion $[AlCl_4]^-$ converts it into an asymmetric ion.[48] The anion $[AlCl_4]^-$ alters also the interatomic distances in the ICl ligand: I(2)–Cl(1) ≠ I(3)–Cl(2). Nevertheless the cation remains planar (Fig.4).

The attempts[49,50] to represent the cation $[Cl(ClF)]^+$ as having a symmetrical structure in which the central atom is fluorine failed. Analysis of the vibrational spectra and quantum-mechanical calculations showed that this cation is asymmetric.[8,22]

Among the penta-atomic cations $[(Hal(Hal')_4]^+$, only compounds of the type $[HalF_4]^+$ (Hal = Cl, Br, or I) are so far known. They have a trigonal-bipyramidal structure (C_{2v} symmetry) with the unshared electron pair in the equatorial plane.[51-53] This structure has been confirmed by X-ray diffraction and NMR. Quantum-mechanical calculations lead to the C_{2v} symmetry only when the *d* orbital of the central atom is used.[54,55] The hepta-atomic cations $[Hal(Hal')_6]^+$ are also known only with fluoride ligands. The octahedral structure of the cations $[ClF_6]^+$, $[BrF_6]^+$, and $[IF_6]^+$ has been explained either by the sp^3d^2 hybridisation of the atomic orbitals of the central atom or by the involvement of all of its three delocalised pairs of *p* electrons in the formation of three polar three-centre four-electron σ-bonds of the *p*–*p* type.[56,57] The high symmetry of the environment of the complex-forming agent has been confirmed by the analysis of ^{129}I Mössbauer,[58,59] NMR,[60,61] and vibrational spectra.[62]

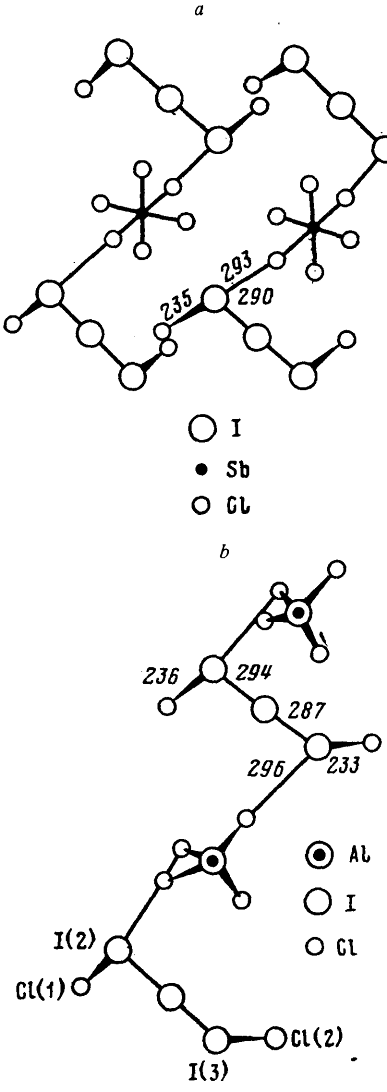

Figure 4. Fragments of the structures of $[I(ICl)_2][SbCl_6]$ (*a*) and $[I(ICl)_2][AlCl_4]$ (*b*)[48] (the interatomic distances are given in pm).

The effective charges on Cl(VII) and Br(VII) in the cations $[ClF_6]^+$ and $[BrF_6]^+$ are respectively +2.998 and +2.859, while those on the ligands are −0.332 and −0.310.[23–25] Most of the halogen cations investigated form crystals belonging to the triclinic and monoclinic systems (Table 1). Almost all the anions, except $[AlCl_4]^-$ and $[BF_4]^-$, have a somewhat distorted octahedral symmetry, ranging from O_h to D_{4h}, owing to the presence of bridging ligands.[17] The octahedral structure of the cations and anions increases the symmetry of the crystal lattice of the halogen cations to the symmetry corresponding to the cubic system (space group P_a3). In particular, $[IF_6][AuF_6]$, $[IF_6][SbF_6]$, $[IF_6][AsF_6]$, $[BrF_6]\cdot[AsF_6]$, and $[ClF_6][PtF_6]$ crystallise in the cubic system with the parameter *a* equal to respectively (pm) 957.3,[8,65] 606.9,[8,66] 949.3,[56,65] 939.4,[8,67] and 939.[68] Only the crystal lattice of $[IF_6][RuF_6]$ has different parameters (space group $P2_1/n$; $a = 981$, $b = 761$, and $c = 580$ pm; $\beta = 107.8°$).[65]

Table 1. Crystallographic characteristics of certain halogen cation compounds.

Compounds	Crystal system*	Space group	Crystal lattice parameters				Refs.
			a, pm	*b*, pm	*c*, pm	angles, °	
$[I_3][AsF_6]$	Tr	$P\bar{1}$	805.4	594.0	1050.3	103.1 (α); 88.9 (β); 100.3 (γ)	[15]
$[I_5][SbF_6]$	Tr	$P\bar{1}$	829	1561	839	81.5 (α); 110.0 (β); 85.5 (γ)	[37]
$[ClF_2][SbF_6]$	Tr	$P\bar{1}$	560	1055	530	92.1 (α); 91.8 (β); 91.5 (γ)	[16]
$[ClF_2][AsF_6]$	M	$A2/_a$	1067.6	767.3	806.4	113.4 (β)	[26]
$[BrF_2][SbF_6]$	Or	P_{cca}	1012	581	1095	—	[17, 18]
$[BrF_2][NbF_6]$	Or	P_{cca}	1006	596	1070	—	[47]
$[BrF_2]_2[GeF_6]$	M	$P2_{1/c}$	507	1382	645	116.6 (β)	[27, 63]
$[ICl_2][SbCl_6]$	T	$P4_1$	698	698	2420	—	[19]
$[ICl_2][AlCl_4]$	M	$P2_1$	692	1102	611	99.1 (β)	[19]
$[ICl_2][SbF_6]$	Or	C_{mca}	1075.1	1208.7	1298.2	—	[42]
$[I(ICl)_2][SbCl_6]$	Tr	$P\bar{1}$	709	1159	713	122.3 (α); 98.0 (β); 115.9 (γ)	[46–48]
$[I(ICl)][AlCl_4]$	M	$C2/_c$	2753	712	1419	110.4 (β)	[48]
$[IBr_2][Sb_2F_{11}]$	Or	P_{bca}	1444.5	1403.4	1272.5	—	[41]
$[I(IBr)_2][SbCl_6]$	Tr	$P\bar{1}$	713	722	775	88 (α); 83 (β); 81 (γ)	[48]
$[I(BrCl)][SbCl_6]$	Tr	$P\bar{1}$	708.4	629.9	1351.1	94.5 (α); 100.3 (β); 92.6 (γ)	[41]
$[BrF_4][Sb_2F_{11}]$	M	—	1419	1450	527	90.6 (β)	[52]
$[IF_4][SbF_6]$	T	$P4/_{nmn}$	589.2	—	1025.5	—	[64]
$[IF_4][Sb_2F_{11}]$	M	$P2/_{1/c}$	852	1482	998	112.7 (β)	[51]

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*Abbreviations for crystal systems: Tr = triclinic, M = monoclinic, Or = orthorhombic, and T = tetragonal.

It is noteworthy that the cation $[BrF_2]^+$ forms with many singly charged anions crystals having almost identical crystal lattices (Table 1). The crystal lattices of $[I(IBr_2)][SbCl_6]$ and $[I(BrCl)][SbCl_6]$ are also very similar despite the different nature of the ligands in the cations. The replacement of the ligands in the anions for the same cation alters sharply the crystal system—cf $[ICl_2][SbCl_6]$ and $[ICl_2][SbF_6]$ in Table 1.

The crystal lattices of the halogen cation compounds consist of infinite chains of cations and anions linked by halide bridges. The compounds are therefore regarded as partly covalent *cis*-bridged polymers.[42] The most important optical constants of the crystals of the halogen cation compounds are still to be determined, but one can already say that the vast majority of the crystals must be optically anisotropic and biaxial.

III. THE ELECTRONIC, VIBRATIONAL, NQR, and NMR SPECTRA

The electronic spectra (Table 2) are mainly used for the identification of the cations from the values of ε, the wavelengths of the absorption band maxima, and the shape of the latter. The bathochromic and hypsochromic effects and the presence of isosbestic points, which might yield information about the number of different cations in solution, have not been investigated. It follows from Table 2 that, for a number of halogen cation compounds, the absorption band in the range 435–470 nm apparently corresponds to the $\Pi^0 \rightarrow \Pi^*$ transitions which should have a low value of ε ($\lg \varepsilon < 3.30$).

Table 2. Electronic spectra of halogen cation compounds in various solvents (298 K).

Cation	HSO_3F		HSO_3CF_3		H_2SO_4 (96%)		Refs.
	λ, nm	lg ε	λ, nm	lg ε	λ, nm	lg ε	
$[Br_3]^+$	292–300 375–380*	— —	— —	—	— —	—	[4,69–72]
$[I_3]^+$	300–305 470–472	3.7 3.2	295 462	3.8 3.4	290 459	3.8 3.3	[7, 30, 36, 73–78]
$[I(IBr)]^+$	260 300* 414–420	3.6 3.3 2.9	260* 300* 418	3.7 3.4 3.0	255–270* 300* 408–490	3.8 3.4 3.1	[77, 78]
$[IBr_2]^+$	232 361 455*	3.7 2.7 ~2.2	260 360 453*	3.1 2.8 2.3	260 355 540–535	3.2 2.8 —	[8, 77–79]
$[I(ICl)]^+$	230 300 461	— 3.1 2.7	235 315 450	— 3.1 2.8	— 295–300 435	— 3.3 2.9	[30, 46, 77, 78, 80]
$[ICl_2]^+$	275* 395 486	2.7 1.8 1.7	310 374 471	2.2 1.8 1.7	318 355* 448	2.1 1.9 1.7	[8, 76–79]

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*There is a low-slope shoulder on the absorption curve.

The electronic spectra of solutions of certain halogen cation compounds have been little investigated. The cation $[I_5]^+$ in solution in HSO_3F is characterised by absorption bands at 240, 270, 345, and 450 nm, while in solution in 96% H_2SO_4 it is characterised by bands at 330 and 450 nm.[8] Absorption bands at 270 nm ($\lg \varepsilon = 3.0$), 340 nm ($\lg \varepsilon = 2.5$), and 488 nm ($\lg \varepsilon = 1.9$) correspond to the cation $[I(BrCl)]^+$ in solution in 96% H_2SO_4.[77,78] The reddish-brown colour of the solution and the appearance of absorption bands at 305 and 470 nm are characteristic of the cation $[I_3]^+$. The absorption band at 440 nm (solution in SO_2 [46]) corresponds to the cation $[I(ICl)_2]^+$, while the bands at 248–252 and 305 nm (solution in SbF_5) correspond to the cations $[BrCl_2]^+$ and $[Br(BrCl)]^+$.[72]

The main information about the vibrational spectra of polycrystalline halogen cation compounds are presented in Tables 3–5. They have been fairly completely analysed by Shamir.[8] It is noteworthy that the assignment of many bands is still obscure. According to Gillespie and Morton[4] and Surles and Quarterman,[88] the band at 384–387 cm^{-1} in the Raman spectrum of the cation $[ClF_2]^+$ corresponds to ν_2 vibrations, while according to Christe and co-workers[39,89] the band at 544 cm^{-1} corresponds to these vibrations. The same discrepancy has been observed also in the assignment of the 537 cm^{-1} band in the IR spectrum of the same cation. The identification of the bands in the vibrational spectra of the cations $[IBr_2]^+$ and $[ICl_2]^+$ is also uncertain.

The angular structure of the triatomic cations has been confirmed not only by the activity of the three normal vibrations ($2A_1 + B_1$) in the IR and Raman spectra but also by the similarity of the ν_1 and ν_3 frequencies. Furthermore, the virtual identity (to within ±10 cm^{-1}) of the vibration frequencies of the halogen cation compounds dissolved in HF and of the crystals of their compounds indicates the presence in the liquid and solid phases of the same discrete ions $[Hal(Hal')_2]^+$.

The frequencies of all nine species of the normal vibrations of the cations $[Hal(Hal')_4]^+$ ($4A_1 + A_2 + 2B_1 + 2B_2$) have been found in the Raman and IR spectra (Table 4). The most intense band in the range 720–820 cm^{-1} corresponds to the symmetrical (ν_1) and antisymmetric (ν_8) equatorial vibrations of the Hal–Hal' bond. The frequencies of the antisymmetric (ν_6, B_1) axial vibrations are apparently identical with the frequencies of the type ν_1 vibrations.

Table 5 shows that $\nu_1 < \nu_2$ for the cations $[BrF_6]^+$ and $[IF_6]^+$, in contrast to $[ClF_6]^+$. This has also been confirmed by quantum-mechanical calculations.[104] In the octahedral ions with heavy complex-forming agents, the fully symmetrical vibration leads to the appearance of polarised lines in

Table 3. Vibrational spectra of triatomic halogen cations.

Cation	Type of spectrum	Frequency, cm^{-1}			Refs.	Cation	Type of spectrum	Frequency, cm^{-1}			Refs.
		ν_1	ν_2	ν_3				ν_1	ν_2	ν_3	
$[Cl(ClF)]^+$	IR	530	290	590	[4, 5, 28, 50, 70]	$[Br_3]^+$	IR	—	—	—	[8, 69, 70]
$[Cl(ClF)]^+$	R	744	535–540	293–299		$[Br_3]^+$	R	290	140	288	
$[ICl_2]^+$	IR	368–370	—	—	[70, 77, 78, 80–83]	$[BrF_2]^+$	IR	705–713	308	695	[5, 44, 70, 87, 88, 92–94]
$[ICl_2]^+$	R	366–371	143–149	350–364		$[BrF_2]^+$	R	704	362	702	
$[I(ICl)]^+$	IR	—	—	—	[46, 70, 77, 84]	$[I_3]^+$	IR	207	114	233	[8, 70]
$[I(ICl)]^+$	R	354–359	124–126	184		$[I_3]^+$	R	207	114	233	
$[Cl_3]^+$	IR	490	225	508	[4, 28, 70, 77, 85]	$[IBr_2]^+$	IR	248	—	258	[41, 77, 78, 82]
$[Cl_3]^+$	R	490	225	508		$[IBr_2]^+$	R	232	123–127	257	
$[ClF_2]^+$	IR	789–805	381–387	815	[5, 39, 44, 70, 86–91]	$[I(BrCl)]^+$	IR	—	—	—	[41, 77, 80, 84]
$[ClF_2]^+$	R	809–811	384	808–830		$[I(BrCl)]^+$	R	242 (I–Br); 362 (I–Cl)	129	250 (I–Br); 356 (I–Cl)	

R = Raman spectrum (Editor of Translation).

the Raman spectrum (ν_1), while lower symmetry vibrations give rise to depolarised scattered radiation (ν_2) and causes the reversal of the frequencies ν_1 and ν_2.[104]

The vibrational spectrum of the cation $[ClF_6]^+$ resembles the spectrum of the isoelectronic SF_6 molecule and the isotopic splitting ($^{35}Cl-^{37}Cl$) of the ν_3 band (890 cm^{-1}), amounting to 13 cm^{-1}, agrees well with the calculated value (12.5 cm^{-1}) for the octahedral structure.[99] In the Raman spectrum of the cation $[ClF_6]^+$, the weak band at 706 cm^{-1}, identified[62] as the $2\nu_6(A_{1g} + E_g + F_{1g} + F_{2g})$ band, is involved in Fermi resonance with the $\nu_1(A_{1g})$ band at 688 cm^{-1} (Table 5).

For the series of cations $[ClF_6]^+$, $[BrF_6]^+$, and $[IF_6]^+$, the stretching force constants f_r are respectively 4.98, 4.90, and 5.42 mdyn A^{-1}.[67] These values are highest for the Cl–F, Br–F, and I–F bonds owing to the high oxidation states of the complex-forming agent.

Extensive investigations of the NQR spectra of the ligand and central atom nuclei established the non-equivalence of the halogen atoms in the cations and the presence of bridge bonds between the cation and anion.[8,105] In particular, analysis of the ^{127}I NQR spectrum of the compound $[I_3][AlCl_4]$ confirmed that one of the iodine atoms in the cation is the complex-forming agent,[30,31] and the cation $[I_3]^+$ should therefore be described by the formula $[I(I)_2]^+$. Furthermore, the dimorphism of $[I_3][AlCl_4]$ has been observed. The frequency 400 ± 5 MHz in the ^{127}I NQR spectrum characterises the complex forming agent in the cation $[I_5]^+ = [I(I_2)_2]^+$.[30]

The frequency of the ^{35}Cl signal in the NQR spectra (at −195 °C) of the halogen cations $[ClF_2]^+$ and $[ClF_4]^+$ is determined, according to the authors,[106,107] by the electron-accepting capacity of the anion. The signal is more intense, the higher the electron-accepting capacity of the anions, which can be arranged in the following sequence in terms of the increase of this capacity: $[TaF_6]^- < [NbF_6]^- < [SbF_6]^- < [AsF_6]^- < [Sb_2F_{11}]^-$. The asymmetry parameter η of the electric field gradient of the complex forming atoms of the cations $[ClF_4]^+$ and $[IF_4]^+$ is 48–50%.[108] After the appearance in the halogen cations of the *cis*-configuration of the Cl–F and I–F bridge bonds with the two SbF_6 octahedra of the $[Sb_2F_{11}]^-$ anions, the values of η and the quadrupole interaction constants diminish somewhat.[108]

Many halogen cation compounds have been investigated by NMR. Two equally intense signals (δ = −256 and −274 p.p.m.), measured relative to $CFCl_3$ at a temperature below −60 °C, in the ^{19}F NMR spectrum of the cation $[ClF_4]^+$ indicate the non-equivalence of the positions of the two fluorine atoms.[53,109,110] which corresponds to a trigonal-bipyramidal structure of the cation and the presence of bridging F atoms. Analysis of the ^{35}Cl and ^{127}I NMR spectra of the cation $[I(ICl)]^+$ established[30,31] that one of the iodine atoms is the complex-forming agent, while the other is the ligand. The angular structure of the cations $[ClF_2]^+$ and $[BrF_2]^+$ [109–112] and the octahedral structure of the cations $[ClF_6]^+$ and $[BrF_6]^+$ [61,99,109,113] have been confirmed.

The ^{129}I Mössbauer spectrum of the cation $[IF_6]^+$ consists of a single signal with the isomeric shift δ = −4.68 mm s^{-1}, which is characteristic of highly symmetrical cations.[8,59]

IV. THERMODYNAMICS OF FORMATION AND DECOMPOSITION

The appearance in solution of the cations $[Hal(Hal')_n]^+$ is not associated with the usual complex-forming reactions and the problem of consecutive equilibria. However, such cations are complex species and enter the ligand substitution, addition, and redistribution reactions characteristic of complex compounds. For example, the following reactions take place in solution in HSO_3F:[77,78]

$$[IBr_2]^+ + Cl_2 \rightleftarrows [ICl_2]^+ + Br_2;\ [IBr_2]^+ + [ICl_2]^+ \rightleftarrows 2[I(BrCl)]^+;$$
$$[I(I)_2]^+ + [ICl_2]^+ \rightleftarrows 2[I(ICl)]^+;\ I(SO_3F) + IBr \rightleftarrows [I(IBr)](SO_3F).$$

Table 4. Vibrational spectra of penta-atomic halogen cations.

Cation	Type of spectrum	Frequency (cm^{-1}) and band assignment								Refs.
		$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(A_1)$	$\nu_5(A_2)$	$\nu_7(B_1)$	$\nu_8(B_2)$	$\nu_9(B_2)$	
$[ClF_4]^+$	IR	799—802	568	515—519	236	474	536	822—830	—	[53, 86, 95, 96]
$[ClF_4]^+$	R	796—803	568	511	—	—	536	826	395	
$[BrF_4]^+$	IR	—	606	—	—	690*	419	730	369	[61, 78, 95, 97]
$[BrF_4]^+$	R	724	604	383	214—219	703*	416—424	736	365—371	
$[IF_4]^+$	IR	728	—	345	—	—	388	719	311	[53, 94, 98]
$[IF_4]^+$	R	729—732	614—621	342	241	655*	385—434	720	316	

*The data refer to the $\nu_6(B_1)$ vibrations.

Table 5. Vibrational spectra of hepta-atomic halogen cations.

Cation	Type of spectrum	Frequency (cm^{-1}) and band assignments						Refs
		$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$	
$[ClF_6]^+$	IR	—	—	890	540—590	—	—	[61, 62, 68, 86, 95, 99, 100]
$[ClF_6]^+$	R	679—689	580—630	—	—	515	706 ($2\nu_6$)	
$[BrF_6]^+$	IR	—	—	775	430	—	—	[60, 61, 67, 101]
$[BrF_6]^+$	R	658	668	—	—	405	—	
$[IF_6]^+$	IR	—	—	793	343	—	250	[4, 56, 57, 65, 66, 102, 103]
$[IF_6]^+$	R	708	732	—	—	340	—	

When the anion is replaced, some of these reactions become impossible under previous conditions. In particular, the reaction

$$I(SO_3CF_3)+Hal_2 \rightleftharpoons [I(Hal)_2](SO_3CF_3)$$

takes place only with participation of $Hal_2 = Br_2$; this is due to the low solubility of $I(SO_3CF_3)$ and its polymeric structure.[77,78]

In the reactions presented above, the more electropositive ligand is always substituted by a more electronegative one and the less electropositive complex-forming agent is replaced by a more electropositive one. Reactions are known[114] in which two ligands are substituted at once:

$$[Cl(ClF)][AsF_6]+Cl_2 \rightleftharpoons [Cl(Cl)_2][AsF_6]+ClF\ ;$$
$$[Cl(ClF)][AsF_6]+SOF_2 \rightleftharpoons [Cl(SOF_2)][AsF_6]+ClF\ .$$

The latter reaction occurs even at −130 °C with 85% yield. The substitution of two ligands is apparently preceded by an elimination reaction with formation of two radical species, $Cl^{\bullet}$ and $F^{\bullet}$, which then combine to form the molecule ClF.

The substitution reactions make it possible to establish the following stability series of the cations:[115,116]

$$[IF_2]^+>[BrF_2]^+>[ClF_2]^+;\ [ICl_2]^+>[BrCl_2]^+>[Cl(Cl)_2]^+.$$

The mechanism of the formation of halogen cation compounds has not been ultimately elucidated. It has been suggested that[6,8,9,117] interhalogen compounds or halogens initially dissociate:

$$2BrF_3 \rightleftharpoons [BrF_2]^+ + [BrF_4]^-;\ 3IBr \rightleftharpoons [I(IBr)]^+ + [IBr_2]^-;$$
$$4ICl \rightleftharpoons [I(ICl)_2]^+ + [ICl_2]^-;\ 3I_2 \rightleftharpoons [I_3]^+ + [I_3]^- \text{ etc.,}$$

According to the data of Surles and Hyman,[93,118] on dissociation of BrF_3 (at 30 °C), the concentration of the ions formed is 0.9 ± 0.1 M. The equilibrium constant for the reaction

$$BrF_3+ClF_3 \rightleftharpoons [ClF_2]^+ + [BrF_4]^-$$

at 25 °C and for a BrF_3 mole fraction of 0.22–0.85 is 1×10^{-4}.[116,119] The introduction of electrophiles and nucleophiles (AsF_5, $SbCl_5$, $AlCl_3$, etc.) shifts the equilibrium towards the formation of halogen cation compounds:

$$[BrF_4]^- + SbF_5 \rightleftharpoons BrF_3 + [SbF_6]^-;\ [ICl_2]^- + AlCl_3 \rightleftharpoons ICl + [AlCl_4]^- \text{ etc.,}$$

In the intermediate stages of the formation of the cations, there is a possibility of the appearance of radical-anions. For example, it has been assumed[120] that the abstraction of electrons from Cl_2 can induce the formation of the planar radical cation $Cl_4^{\dot{+}}$ from $Cl_2^{\dot{+}}$ and Cl_2 (weak $\pi-\pi^*$ interaction).

In our view, another mechanism for the formation of halogen cation compounds is also possible:

$$BrF_3+SbF_5 \rightleftharpoons BrF_3\cdot SbF_5 \rightleftharpoons [BrF_2][SbF_6]\ .$$

According to this scheme, an adduct without a rigid nuclear configuration is formed initially and then bridge bonds arise between BrF_3 and SbF_5 as a result of the migration of the nuclei and the redistribution of electron density by virtue of the low activation energy. After this, the fluoride ion is transferred.

The calorimetric method has not so far come to be widely used in the study of the formation reactions of halogen cation compounds. Systematic investigations in this field are only just beginning. In particular, the enthalpies of solution (at 25 °C) of SbF_5, SnF_4, and TaF_5 in BrF_3, which represent the overall energies of the dissolution process and the chemical reaction, are respectively −92.3 ± 0.3, −58.8 ± 0.7, and −45.2 ± 0.8 kJ per mole of the dissolved fluoride.[119] On the other hand, the enthalpies of formation ($-\Delta H^0_{298}$) of $[BrF_2][SbF_6]$, $[BrF_2]_2[SnF_6]$, and $[BrF_2][TaF_6]$ are respectively 1773, 1505, and 2251 kJ mol^{-1}. The last quantity includes ΔH^0_{298} for the formation of BrF_3 and TaF_5. On the other hand, the enthalpies of solution of the same halogen cation compounds in BrF_3 at 25 °C are respectively −4.94, −2.00, and −1.40 kJ mol^{-1}.[119] For the reaction

$$K[BrF_4]+[BrF_2][SbF_6]=K[SbF_6]+2BrF_3\ ,$$

in BrF_3, $\Delta H^0_{298} = -19.1 \pm 1.0$ kJ mol^{-1}. With increase of the degree of solvolysis of the interacting substances, this quantity diminishes and amounts to −15.3 ± 0.8 kJ mol^{-1} for the same reaction involving $[BrF_2][TaF_6]$.[119]

The thermal stabilities of the halogen cation compounds are different. Whereas the compounds containing the cation $[Cl_3]^+$ decompose fully at 25 °C, $[Br_3][AsF_6]$ dissociates only above 70 °C with evolution of Br_2, while in an atmosphere of nitrogen it sublimes without decomposition at 30–50 °C.[71] The halogen cation compounds $[I_3][AlCl_4]$ and $[I_3](SO_3F)$ melt congruently at 45° ± 1 °C[30,31] and at 92–101 °C[38,74] respectively.

Table 6 presents certain thermodynamic characteristics of the thermal decomposition reactions.

$$[Hal(Hal')_n][MHal'_m] \rightleftharpoons Hal(Hal')_{n+1}+MHal'_{m-1}\ .$$

The enthalpies of the thermal dissociation reactions ΔH^0_g, listed in Table 6, were found from the slopes of the $\lg p = f(1/T)$ curves subject to the condition that the enthalpies of sublimation of the test substances are zero.

Table 6. Certain thermodynamic characteristics of the thermal dissociation of halogen cation compounds.

Substance	$\lg p$ (mmHg)	T, K	ΔH^0_g, kJ mol^{-1}	$-\Delta H^0_{298}$, kJ mol^{-1}	Refs.
$[ClF_2][BF_4]$	$\frac{-2576+16}{T}+(12.00\pm0.06)$	243–293	98.7	1394.5	[14, 89, 121]
$[ClF_2][PF_6]$	$-1798/T+10.53$	—	68.6	1827.1	[8, 14, 89]
$[Cl(ClF)][AsF_6]$	$-2391.6/T+11.71$	209–255	137.2	1487	[50]
$[BrF_2][SbF_6]$	$-3030/T+7.66$	498–623	116.3	1773*	[12, 119, 122]
$[ClF_4][AsF_6]$	$-2763.6/T+12.2$	242–283	105.6	1576.5	[123]
$[IF_6][AsF_6]$	$-4800/T+16.42$	—	183.7	2251	[56]

Notation: p is the thermal dissociation pressure and ΔH^0_g the enthalpy of thermal dissociation.

*Found from calorimetric measurements.[119]

The complex $[ClF_2][BF_4]$ dissociates fully into ClF_3 and BF_3 in the gas phase at temperatures above 30 °C, while $[Cl(ClF)][BF_4]$ decomposes already at temperatures above −112 °C and in the liquid state this substance is unknown.[50] The products of the thermal decomposition of the complex $[Cl(ClF)][AsF_6]$ are gaseous ClF and AsF_5. $\Delta G^0_T = 9.0$ kJ mol^{-1} and $\Delta S^0_T = 491.2$ J mol^{-1} K^{-1} for this reaction.[50] The enthalpy of the thermal dissociation of $[BrF_2][SbF_6]$ in the range 130–350 °C, calculated from vapour pressure data, is 116.3 kJ mol^{-1}, while the calorimetric value is 186 kJ mol^{-1}.[119] The thermal dissociation pressure of $[BrF_2][BF_4]$ at −31 °C is 4 mmHg, while at 23 °C the halogen cation compound decomposes fully.[124]

The stability of the complexes with the cation $[IF_2^+]$ increases in the series of anions $[BF_4]^- < [AsF_6]^- < [SbF_6]^-$. Whereas the compound $[IF_2][BF_4]$ is stable only in solution of acetonitrile, the compound $[IF_2][SbF_6]$ withstands heating to 45 °C.[125,126] $\Delta G^0_T = 2.9$ kJ mol^{-1} and $\Delta S^0_T = 344.3$ J mol^{-1} K^{-1} have been found[123] for the reaction

$$[ClF_4][AsF_6](\text{cryst.}) = ClF_5(\text{gas}) + AsF_5(\text{gas})$$

The products of the dissociation of $[ClF_4][PtF_6]$ above 25 °C (the vapour pressure at 23 °C is 2 mmHg) are ClF_5, PtF_4, and PtF_6.[91]

The thermal decomposition of substances containing the cation $[ClF_6]^+$ is accompanied by the evolution of fluorine.[62,100] The complex $[ClF_6][PtF_6]$ dissociates above 140–180 °C,[68] while $[IF_6][AsF_6]$ sublimes at 120–140 °C with decomposition into IF_7 and AsF_5 ($\Delta G_T^0 = 32.6$ kJ mol^{-1} and $\Delta S_T^0 = 506.3$ J mol^{-1} K^{-1}).[56,127]

Among the known compounds of the hexafluoride (VII), the complex $[IF_6][BF_4]$ is the least stable, the vapour pressure amounting to 10 mmHg at −60 °C.[127]

V. SYNTHESIS OF HALOGEN CATION COMPOUNDS

The methods of synthesis of halogen cation compounds are based mainly on reactions between interhalogen compounds and halogens and the halides of Group IIIA–VA elements in their highest oxidation states. The halogen cation compounds obtained by one or other preparative method but having the same compositions can exhibit appreciably different melting points[8] and other physical characteristics, which is due to the presence of admixtures of the initial reactants and side products of the reaction. The degree of contamination is reduced only after carrying out the synthesis within the limits of the region of crystallisation of the target products, determined from the phase diagrams of the corresponding systems.

The cation $[Cl(Cl)_2]^+$. The appearance of a phase containing $[Cl_3]^+$ has been observed in the systems Cl_2–ClF–AsF_5 (SbF_5, $SbCl_5$, HF) at −76 °C and below,[4,7,28,70] in the system $[Cl(ClF)][AsF_6]$–Cl_2 at −78 °C,[28] and in the system Cl_2–$SbCl_3$ at −51 °C.[128] The formation of the cation $[Cl_3]^+$ has not been observed in the systems HSO_3F–SO_3–Cl_2–$SbCl_5$ (25 °C, 3 atm)[85] and ClF–Cl_2–BF_3 (at temperatures from 130° to 25 °C).[4,7]

The cation $[Br(Br)_2]^+$. When BrF_5 and Br_2 are condensed in a quartz reactor containing a 30% excess of $AsF_5(SbF_5)$ at −196 °C, brown crystals are formed[71] via the reaction

$$7Br_2+BrF_5+5AsF_5=5[Br_3][AsF_6]\ .$$

The reaction,[71,129]

$$2O_2[AsF_6]+3Br_2=2[Br_3][AsF_6]+2O_2\ .$$

leads to the same result. In order to avoid the formation of the cation $[Br_2]^+$, the molar ratio Br_2/BrF_5 in the first reaction should not exceed 4.5.[72]

The appearance of the cation $[Br_3]^+$, noticed in a number of investigations[4,7,29,70,130,131] in the systems Br_2–$S_2O_6F_2$ (SbF_5, HSO_3F, SO_3) is caused by reactions of the type

$$3Br_2+S_2O_6F_2\rightleftharpoons2[Br_3]^++2SO_3F^-\ .$$

The cations $[I(I)_2]^+$ *and* $[I(I_2)_2]^+$. The formation of new phases with the cations $[I_3]^+$, $[I_5]^+$, and $[I_7]^+$ has been postulated in the systems I_2–$S_2O_6F_2$ [38] and I_2–ICl–$AlCl_3$.[30,31] These phases could not be isolated from the melt. Spectroscopic analysis (^{19}F NMR, IR) of the liquid phases failed to confirm the formation of the cations $[I_3]^+$ and $[I_7]^+$ in the first system. The results of cryoscopic measurements for the same system are contradictory and do not lead to unambiguous conclusions.[38,75,132]

The black-brown powder of $[I_3](SO_3F)$ was obtained[74] only after prolonged treatment of an excess of I_2 with pure $S_2O_6F_2$ at 20 °C with subsequent heating of the mixture to 85 °C and cooling to −180 °C. The possibility of the synthesis of the complex has been pointed out in several investigations.[4,36,133] At a low temperature the interaction of I_2 and $S_2O_6F_2$ leads to formation of the diamagnetic cation $[I_4]^{2+}$ together with $[I_3]^+$,[4,35,36,134] while according to a number of other data[7,29,75] the cation $[I_5]^+$ is also formed.

The compounds $[I_3][AsF_6]$,[15,135] $[I_5][SbF_6]$,[37] and $[I_7]\cdot[SO_3F]$[38] have been obtained in a crystalline state by purely preparative methods. The composition of the last phase requires confirmation.

The results of the study of the systems I_2–HIO_3 (KI, ICI, I_2O_5)–H_2SO_4($HSClO_3$, $K_2S_2O_8$) by conductimetric titration methods, the reddish-brown colour of the solutions, and the electronic spectra indicate the formation of the cation $[I_3]^+$.[1,73,76,133,136] It has been suggested that the cation $[I_3]^+$ should also be formed in the systems I_2–$H_2S_2O_7$,[137] I_2–HSO_3F,[138] I_2–SO_2–SbF_5,[70] ICl–H_2SO_4, I_2–HCl–BCl_3–$K_2S_2O_8$, I_2–CF_3COOH–BF_3–$K_2S_2O_8$, and ICl–BF_3–CF_3COOH.[136] The cation $[I_5]^+$ has been detected in the systems I_2–HIO_3–H_2SO_4 with a molar ratio $I_2/HIO_3 > 7$,[73,133] and also in the systems I_2–H_2SO_4–SO_3 [139] and I_2–SbF_5–AsF_3.[37,140]

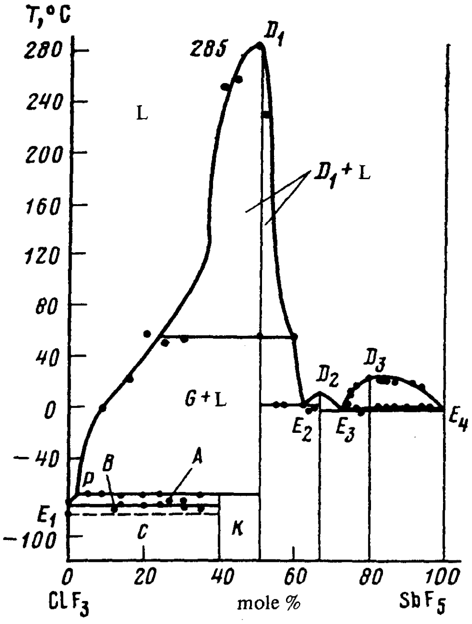

Figure 5. Phase diagram for the system ClF_3–SbF_5:[141] D_1 = α-$[ClF_2][SbF_6]$; D_2 = $ClF_3.2SbF_5$; D_3 = $ClF_3.4SbF_5$; G = β-$[ClF_2][SbF_6]$; P = $3ClF_3.2SbF_5$; A = $3ClF_3.2SbF_5$ + L; B = $3ClF_3.2SbF_5$ + α-ClF_3; C = $3ClF_3.2SbF_5$ + β-ClF_3; L = liquid phase; K = $3ClF_3.2SbF_5$ + β-$[ClF_2][SbF_6]$.

The cation $(ClF_2)^+$. A thorough study[141] of the system ClF_3–SbF_5 (Fig.5) showed that the interaction of its components can result in the formation of not only $[ClF_2][SbF_6]$ and $[ClF_2][Sb_2F_{11}]$ but also of two new phases: $3ClF_3.2SbF_5$ (P) and $ClF_3.4SbF_5$ (D_3). The coordinates of the eutectic points are E_1 = 98 mol% ClF_3, m.p. −72 °C; E_2 = 37.95 mol%, 2 °C; E_3 = 27.50 mol%, 0 °C; E_4 = 1.2 mol%, +7 °C. The compound $[ClF_2][SbF_6]$ is dimorphic with a phase transition temperature of 55 °C. The congruent melting points of the phases D_2 and D_3 are respectively 11° and 25 °C.

Compounds with the cation $[ClF_2]^+$ are synthesised either by condensing ClF_3 on AsF_5 {SbF_5, BF_3, PtF_6, $O_2[PtF_6]$} at −196 °C with subsequent removal of the excess ClF_3 in a stream of nitrogen or by the direct reaction of ClF_3 with AsF_3 (SbF_3, BF_3), which proceeds vigorously even at −70 °C. The excess ClF_3 can convert the chlorides or fluorides of the elements in the lowest oxidation state initially into Lewis acids and then into compounds with the cation $[ClF_2]^+$.[127,142] The compounds $[ClF_2][SbF_6]$,[16] $[ClF_2][AsF_6]$,[26,89,127,143] $[ClF_2][BF_6]$,[12,14,89,121] and $[ClF_2][PtF_6]$ [90,144–146] were obtained in this way in the crystalline state. The individuality of some of these compounds is open to doubt, in particular the melting point data[127,142] for $[ClF_2][SbF_6]$ (75–78 °C) differ by 207–210 °C from those in another study[141] (Fig.5).

The synthesis of $[ClF_2][IrF_6]$ and $[ClF_2][PF_6]$ has been reported.[12,26] The system ClF_6–HF is of the eutectic type (44% ClF_3, m.p. −110.7 °C),[9,12,88,147] although the cations $[ClF_2]^+$ have also been detected in solution.[88,148] The components of the ClF_3–UF_6 system do not interact either.[9,149]

The cation [Cl(ClF)]⁺. Using the synthetic methods described above, the compound $[Cl(ClF)][AsF_6]$, which is stable below −70 °C, was obtained.[50] In solution in the HF–SbF_5 mixture, the cation decomposes even at −76 °C.[4,28]

The cation [BrF₂]⁺. The formation of not only $[BrF_2]$.$[SbF_6]$ (m.p. 129 °C) but also of a series of other new phases, namely $BrF_3.3SbF_5$ (m.p. 33.5 °C), $3BrF_3.2SbF_5$, and $3BrF_3.SbF_5$ has been established in the system BrF_3–SbF_5 (Fig.6). The incongruent melting points of the last two phases are respectively 30.8° and −16.3 °C.[150]

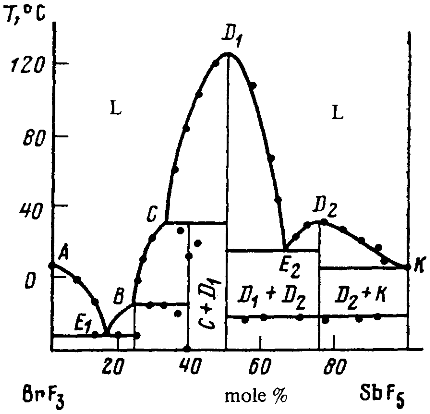

Figure 6. Phase diagram for the system BrF_3–SbF_5;[150] $D_1 = [BrF_2][SbF_6]$; $D_2 = BrF_3.3SbF_5$; $A = BrF_3$; $B = 3BrF_3.SbF_5$; $C = 3BrF_3.2SbF_5$; $K = SbF_5$. Coordinates of the eutectic points: E_1 = 83.0 mole % BrF_3, m.p. 33.1 °C; E_2 = 33.5 mole % BrF_3, m.p. 15 °C.

The formation of the compound $[BrF_2]_2[SnF_6]$, melting incongruently at 93° ± 1 °C, has been observed[151] in the system BrF_3–SnF_4, which has been only partly investigated owing to the high viscosity of the melt. The formation of two incongruently melting phases has been established in the BrF_3–PtF_4 system:[152] $[BrF_2]_2[PtF_6]$ and $7BrF_3.PtF_4$.

A whole series of compounds with the $[BrF_2]^+$ cations have been obtained, incorporating the following anions apart from those indicated above: $[AsF_6]^-$,[92] $[BF_4]^-$,[63,124,153] $[NbF_6]^-$, $[TaF_6]^-$, $[BiF_6]$,[17,154,155] $[GeF_6]^{2-}$,[27,63,92] $[PdF_4]^-$, $[RuF_6]^-$, $[AuF_4]^-$, and $[RhF_6]^-$.[154,156–159] The data concerning the synthesis[153] of $[BrF_2][BF_4]$, allegedly stable at room temperature, were not confirmed.[124] The interaction of BrF_3 and BF_3 affords the compounds $[BrF_2][BF_4]$ (stable below −80 °C) and $[BrF_2][B_2F_7]$ (stable below −120 °C).[63,124] The separation of these compounds without the preliminary study of the system BrF_3–BF_3 is very difficult.

The above halogen cation compounds are synthesised by the methods involving the direct interaction of the fluorides, chlorides, and oxides of the elements with an excess of BrF_3. The residual BrF_3 is then removed *in vacuo*.[92,160–162] The reaction with the oxides proceeds vigorously and is accompanied by the evolution of O_2, Br_2 being introduced into the reactor to slow it down.

The method involving the direct interaction of BrF_3 with powdered metals at temperatures ranging from 190 °C and above has also been recommended.[155,156,158,159,161,163] For platinum metals, a mixture of BrF_5 and Br_2 is used instead of BrF_3.[164] The reactions of BrF_3 with SO_3, $Br(SO_3F)_3$, and $F(SO_3F)$, and of BrF_5 with SO_3 result in the formation of the same compound $[BrF_2](SO_3F)$.[111,165]

The cations [BrCl₂]⁺ and [Br(BrCl)]⁺. They exist only in liquid phases of the systems Cl_2–$Br(SO_3F)$–SbF_5 and Cl–$Br_2(Sb_3F_{16})$.[72]

The cation [IF₂]⁺. It is formed in the systems IF_3–BF_3–CH_3CN (at −45 °C) and $I(SO_3F)$–SO_3F_2.[12,74] The interaction of IF_3 with $AsF_5(SbF_5)$, cooled to −78 °C, results in the formation in the solid state of $[IF_2][AsF_6]$ (decomposes at −22 °C) and $[IF_2][SbF_6]$, which can withstand heating to 45 °C.[125,126]

The cation [ICl₂]⁺. It forms red and orange-red crystals with the anion SO_3F^- when $I(SO_3F)$ is acted upon by liquid chlorine (at −70 °C) with subsequent increase of temperature to 20 °C [74,77,82] or when a suspension of I_2Cl_6 in CCl_4 (below −10 °C) is mixed with a limited amount of SO_3.[166,167] The compounds of dichloroiodine (III) have been obtained with the following anions: $[SbF_6]^-$—by adding I_2Cl_6 to a solution of SbF_5 in SO_2ClF with subsequent removal of the excess SO_2ClF by slow distillation;[42] $[Sb_2F_{11}]^-$—by the reaction of I_2Cl_6 with SbF_5;[78] $[SbCl_6]^-$—by the reaction of I_2Cl_6 with an excess of $SbCl_5$ at 100 °C [19,81,83,168] or on mixing I_2, $SbCl_5$, and an excess of liquid chlorine (at −196 °C) with subsequent raising of the temperature to −80 °C;[80,84,169] $[AlCl_4]^-$—by heating equimolar amounts of I_2Cl_6 and $AlCl_3$ in CCl_4 or $CHCl_3$ [19,81,168,169] and also by the reaction of I_2Cl_6 with $AlCl_3$ in a sealed tube at 100 °C.[83]

The cation [I(ICl)]⁺. It follows from the phase diagram for the system ICl–$AlCl_3$ [30,170] that the reaction of ICl with $AlCl_3$ leads to the formation of the compound $2ICl.AlCl_3$ = $[I(ICl)][AlCl_4]$, melting incongruently at 53 °C, in which the ligands are the I^- and Cl^- ions. Signs of the appearance of an analogous compound have been observed[171,172] also in the system ICl–$AlCl_3$–$C_6H_5NO_2$. According to Pohl and Saak,[48] only the compound $[I(ICl)_2][AlCl_4]$ is formed in the reaction of ICl with $AlCl_3$. The reaction

$$I_2 + 2SbCl_5 \rightleftharpoons [I(ICl)][SbCl_6] + SbCl_3 .$$

is apparently possible in the system I_2–$SbCl_5$.[140,173–176] The dark-brown crystals of $[I(ICl)][SbCl_6]$ have been obtained by the interaction of ICl and $SbCl_5$ and of I_2, $SbCl_5$, and

Cl_2 (at −196 °C).[47,70,80,84] It has been suggested[8,80] that the last reaction is followed by the side process

$$I_2+Cl_2 \rightleftharpoons 2ICl$$

which initiates the reaction

$$ICl+Cl_2+SbCl_5=[ICl_2][SbCl_6] \ .$$

It is believed[8] that the nI_2 + ICl + $SbCl_5$ interaction (n = 1–3) always entails the formation of the cation $[I(ICl)]^+$ in the first stage regardless of the ratio of the initial components, pressure, and temperature.

The formation of two compounds, namely $[I(ICl)][SbCl_6]$ and $[I(ICl)_2][SbCl_6]$, melting congruently at almost the same temperature (62.5 °C), has been established in the system $ICl–SbCl_5$.[177] Whereas the compound $[I(ICl)]$.$[GaCl_4]$, melting incongruently at 28.5 °C, is formed in the system ICl–GaGl,[173] the only product in the system ICl–$SbCl_3$ is the adduct $SbCl_3$.5ICl [178] (ICl.$SbCl_3$ is formed according to other data[173,179]). No interaction has been observed between ICl and $AsCl_3$.[180] Similarly only the adduct ICl.$TaCl_5$, melting incongruently at approximately 102 °C, is formed in the system ICl–$TaCl_5$, while the system ICl–$NbCl_5$ is of the purely eutectic type.[181]

The reactions of $I(SO_3F)$ and ICl (at 50 °C) and of $[I_3]$.(SO_3F) and $[ICl_2](SO_2F)$ in a stream of dry nitrogen[77,78] lead to the formation of $[I(ICl)](SO_3F)$.

The cation $[I(ICl)_2]^+$. The mechanism of reactions in which the ICl molecules become the ligands while iodine acquires the +1 oxidation state has not been ultimately elucidated. Thus the reaction of ICl with $SbCl_5$ or $AlCl_3$ entails the formation, together with the cation $[I(ICl)]^+$, also of the cation $[I(ICl)_2]^+$.[48,174,182,183] According to other data,[46,47] the compound $[I(ICl)_2][SbCl_6]$ can also cyrstallise from a solution of I_2Cl_6 and $SbCl_3$ in SO_2.

The cation $[IBr_2]^+$. Compounds with this cation cannot be obtained by the direct interaction of Lewis acids (SbF_5, AsF_5, $AlCl_4$, etc.) with IBr_3 or I_2Br_6, since the latter have not so far been obtained. For this reason, $[IBr_2][Sb_2F_{11}]$ is synthesised in the following manner. A solution of SbF_5 in SO_2 is mixed initially with IBr until the appearance of a precipitate of SbF_5, which is filtered off and SO_2 is removed; the final product is extracted from the paste-like residue with SO_2ClF.[41] The same compound can be obtained in the exchange reaction of $[IBr_2](SO_3F)$ with a large excess of SbF_5 on heating to 70 °C.[78] Compounds with the anions SO_3F^- and $SO_3CF_3^-$ are formed on heating to 50 °C a mixture of $I(SO_3F)$ or $I(SO_3CF_3)$ with Br_2.[77,78,82]

The cation $[IBr_2]^+$ has been detected in the system $I_2–Br_2–HIO_3–H_2SO_4$ at 25 °C with the molar ratio I_2/HIO_3 = 2.0.

The formation of the cations $[IBr_2]^+$ has not been established in the systems IBr–$AlBr_3$,[184] IBr–$GaBr_3$,[173] IBr–$SbBr_3$,[178] and IBr–$AlBr_3(SbBr_3)$–$C_6H_5NO_2$.[182,185] The adduct IBr.$AlBr_3$ was isolated in the first system.

The cations $[I(IBr)]^+$ and $[I(IBr)_2]^+$. When $I(SO_3F)$ and IBr interact (at 50–75 °C), the compound $[I(IBr)](SO_3F)$, melting incongruently at 70 °C, crystallises,[77] while the almost black crystals of $[I(IBr)_2][SbCl_6]$ can be obtained by the reaction of ICl, IBr, and $SbCl_5$.[48] Both cations apparently exist in the same systems and their crystallisation regions are determined by the ratio of the components, as in the systems of the cations $[I(ICl)]^+$ and $[I(ICl)_2]^+$.

The cation $[I(BrCl)]^+$. It enters into the composition of two compounds: $[I(BrCl)][SbCl_6]$ and $[I(BrCl)](SO_3F)$. The first was obtained[41,80] by the interaction of IBr, Cl_2, and $SbCl_5$ in SO_2 (at −78 °C) and the second by mixing equimolar amounts of $[IBr_2](SO_3F)$ and $[ICl_2](SO_3F)$ at 95 °C.[78] It is believed[33,41] that this entails the formation of a disordered mixture of the cations $[IBr_2]^+$, $[ICl_2]^+$, and $[I(BrCl)]^+$ which are in equilibrium

$$2[I(BrCl)]^+ \rightleftharpoons [IBr_2]^+ + [ICl_2]^+.$$

The cation $[ClF_4]^+$. The study of the system ClF_5–SbF_5 (Fig.7) led to the observation[186] of three new congruently melting phases containing the cation $[ClF_4]^+$: $[ClF_4]$.$[SbF_6]$ (m.p. 120 °C), $[ClF_4][Sb_2F_{11}]$ (m.p. 64 °C), and $[ClF_4][Sb_4F_{11}]$ (m.p. 62 °C), the last two compounds having very small crystallisation regions. The first compound has two polymorphic modifications (α and β) with a phase transition temperature of approximately 40 °C. The melting point data,[52,123] for the compound $[ClF_4][SbF_6]$, obtained by preparative synthesis, disagree with the more accurate data.[186] It has been established that HF cannot be used as the solvent for the synthesis of this compound.[186] The system ClF_5–HF is distinguished by the complete absence of the miscibility of the components in both liquid and solid states.[187]

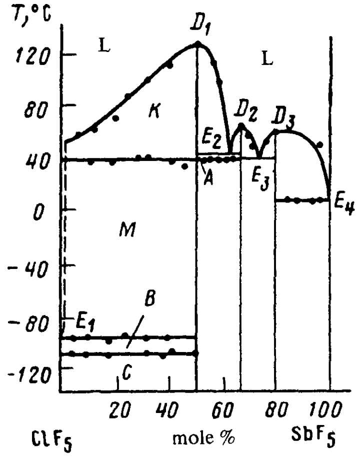

Figure 7. Phase diagram for the system ClF_5–SbF_5:[186] D_1 = $[ClF_4][SbF_6]$; D_2 = $[ClF_4][Sb_2F_{11}]$; D_3 = $[ClF_4]$.$[Sb_4F_{21}]$; A = α-$[ClF_4][SbF_6]$ + $[ClF_4][Sb_2F_{11}]$; B = β-$[ClF_4][SbF_6]$ + α-ClF_5; C = β-$[ClF_4][SbF_6]$ + β-ClF_5; K = α-$[ClF_4][SbF_6]$ + L; M = β-$[ClF_4][SbF_6]$ + L.

The synthesis of $[ClF_4][AsF_6]$ and $[ClF_4][PtF_6]$ is based on the repeated heating and cooling of a mixture of ClF_5 and $AsF_5(PtF_6)$ in the temperature range between −196° and +20 °C.[91,123] The system ClF_5–BF_3 is characterised by the absence of miscibility of the components in both liquid and solid states over the entire concentration range.[188]

The cation $[BrF_4]^+$. In contrast to the previous system, the interaction of BrF_5 and SbF_5 leads to the formation of five new phases (Fig.8), among which only one, $[BrF_4]$.$[Sb_2F_{11}]$, melts congruently (at 81 °C).[189] The low melting point (60–61 °C) observed for this phase elsewhere[113,190] is caused by the presence of impurities.

A general method of synthesis of compounds of halogen cations, incorporating the ion $[BrF_4]^+$, involves the condensation of BrF_5 at −196 °C in a reactor containing the fluorides or oxides of the elements in the highest oxidation states with subsequent alternate heating and cooling of the reactor. In the last stage of the synthesis, the excess BrF_5 is removed *in vacuo*. The cation halogen compound of tetrafluorobromine (III) with the anions $[Sb_2F_{11}]^-$,[53,61,97] $[AsF_6]^-$,[53] $[SnF_6]^{2-}$,[9,192] and $[RuF_6]^-$ [12] (all in the crystalline state) and also with the anions SO_3F^- [190] and $[PtF_6]^-$ [90,91] (in the form of viscous liquids which do not crystallise at low temperatures) were obtained in this way.

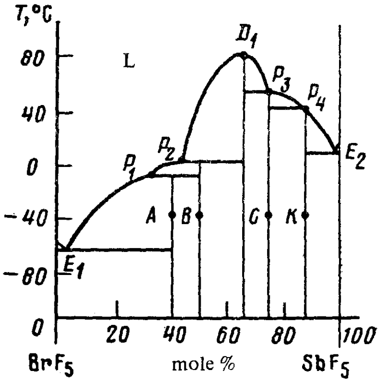

Figure 8. Phase diagram for the system BrF_5–SbF_5:[189] D_1 = dystectic composition $[BrF_4][Sb_2F_{11}]$ (m.p. 81 °C); m.p. of peritectic phases (°C): $P_1 = -8$; $P_2 = 0$; $P_3 = +50$; $P_4 = +40$; E_1, E_2 = eutectic points; $A = 3BrF_5.2SbF_5$; $B = BrF_5.SbF_5$; $C = BrF_5.3SbF_5$; $K = BrF_5.7SbF_5$.

The formation of the cation $[BrF_4]^+$ has not been established in the systems BrF_5–BF_3(NbF_5, BiF_5),[8,97,188] BrF_5–PF_5(TiF_4),[113] BrF_5–UF_6,[9,149] and BrF_5–HF.[9,12,22,88]

The cation $[IF_4]^+$. When IF_5 and SbF_5 interact, three new phases appear (Fig.9):[192] the congruently melting $[IF_4].[SbF_6]$, the incongruently melting $[IF_4][Sb_2F_{11}]$, and the $IF_5.6SbF_5$ phase whose nature has not been elucidated.

The method of synthesis of the majority of the cation halogen compounds with the cation $[IF_4]^+$ is analogous to that used for $[BrF_4]^+$. The compound $[IF_4][CrF_4.Sb_2F_{11}]$ has been synthesised[98] by the reaction in liquid IF_5 at 60 °C (yield 100%):

$$3IF_5+2O_2[CrF_4\cdot Sb_2F_{11}]=[IF_4][CrF_4\cdot Sb_2F_{11}]+2O_2+IF_7\ .$$

The compound decomposes at 153 °C. Compounds with the anions $[SbF_6]^-$,[53,64,108,115,192,193] $[Sb_2F_{11}]^-$,[51] $[PtF_6]^-$,[144,145] and $[CrF_4.Sb_2F_{11}]^-$ [8,98] have been obtained in the crystalline state. The compound $[IF_4](SO_3F)$ is formed in the liquid.[193]

The system IF_5–HF is the eutectic type,[194] the cations $[IF_4]^+$ being detected only in the liquid phase.[9,194]

The cation $[ClF_6]^+$. The synthesis of the cation halogen compounds with the cation $[ClF_6]^+$ proved to be possible only[62] when a powerful oxidant, such as KrF_2, is used under the conditions of cyclic heating from −196° to +20 °C and cooling:

$$ClF_5+KrF_2+AsF_5=[ClF_6][AsF_6]+Kr\ .$$

The excess ClF_5 used as a solvent increases the yield of the complex, which crystallises without an admixture of the cations $[ClF_4]^+$. The compound $[ClF_6][SbF_6]$ was obtained analogously. The synthesis of $[ClF_6][BF_4]$ is possible only via the exchange reaction of $[ClF_6][AsF_6]$ and $Cs[BF_4]$ in HF on raising the temperature from −196° to +25 °C and subsequent cooling of the mixture to −78 °C.[100] The $Cs[AsF_6]$ residue is separated and $[ClF_6][BF_4]$ is crystallised from the filtrate in 55% yield. The synthesis of $[ClF_6][AuF_6]$ is believed to be possible.[195] According to a series of data,[68,86,99]

$$2ClF_5+2PtF_6=[ClF_6][PtF_6]+[ClF_4][PtF_6]$$
$$6ClO_2F+6PtF_6=[ClF_6][PtF_6]+5(ClO_2)[PtF_6]+O_2$$

take place when mixtures of the reactants are heated slowly from −196° to +25 °C with simultaneous UV irradiation (water–Pyrex filter) for several days. The reaction products could not be fully separated.

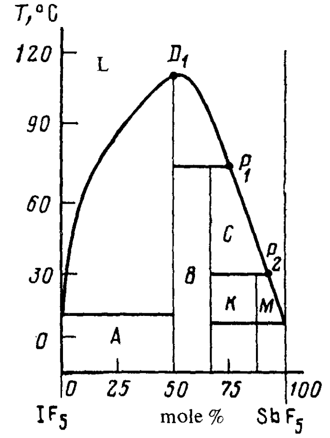

Figure 9. Phase diagram for the system IF_5–SbF_5:[192] D_1 = dystectic composition $[IF_4][SbF_6]$ (m.p. 111 °C); P_1 and P_2 = the peritectic phases $[IF_4][Sb_2F_{11}]$ (m.p. 72 °C) and $IF_5.6SbF_5$ (m.p. 27 °C) respectively; $A = IF_5 + [IF_4].[SbF_6]$; B = mixture of the solid phases D_1 and P_1; $C = [IF_4][Sb_2F_{11}] + L$; $M = IF_5.6SbF_5 + L$; K = mixture of the solid phases P_1 and P_2.

The interaction of the components in the systems ClF_5–F_2–SbF_5(AsF_5) and ClF_5–F_2–BF_3 was not observed at pressures in the range 30–40 atm and temperatures in the range 100–225 °C.[86] Instead of the oxidation of ClF_5 to ClF_7, the former decomposes to ClF_3 and Cl_2 with formation of compounds having the cation $[ClF_2]^+$.

The cation $[BrF_6]^+$. The attempts to synthesise compounds with the above cation by mixing BrF_5, F_2, and AsF_5(SbF_5) were unsuccessful despite the use of increased pressures (125–200 atm) and temperatures (200–250 °C) and varying the molar ratios of the components. Only when a new powerful oxidant KrF_2 was employed, was it possible[60,61,67] to synthesise $[BrF_6][AsF_6]$ and a mixture of $[BrF_6][Sb_2F_{11}]$ with $[BrF_4][Sb_2F_{11}]$. The latter compound is removed from the mixture *in vacuo* at 50 °C. However, after this operation, the composition of the residual cation halogen compounds becomes indefinite:[67] $[BrF_6][SbF_6].xSbF_5$ ($x < 1$). The reaction involving KrF_2 proceeds in BrF_5 at −196 °C. The excess BrF_5 and KrF_2 are removed by evacuation. The yield of the halogen cation compounds with the ion $[BrF_6]^+$ does not exceed 20%. The reasons for the formation of $[BrF_6][Sb_2F_{11}]$ instead of $[BrF_6][SbF_6]$ remain obscure.

The cation $[IF_6]^+$. Cation halogen compounds containing the anions $[AsF_6]^-$,[6,9,12,56,127,196–198] $[SbF_6]^-$,[66] $[Sb_3F_{16}]^-$,[12,127,197,198] $[BF_4]^-$,[6,127] $[BF(TeOF_5)_3]^-$,[199] and $[AuF_6]^-$ [65] have been obtained with this cation.

A general method of synthesis of the compounds is joint condensation in a single reactor at −196 °C of the initial reactants with subsequent increase of temperature to 0 °C; the remaining reactants are removed by evacuation.[56,59,127,200,201] If one of the reactants $[IF_7)$ boils before the other (SbF_5) becomes liquid, then the reaction is carried out by passing gaseous IF_7 through a melt of SbF_5 at 20 °C.[127] The structure of $[IF_6][Sb_3F_{16}]$ has not been ultimately elucidated.

A reaction which takes place even at 20 °C but leads to the formation of a mixture of two solid phases has been proposed for the synthesis of the compound with the anion $[AuF_6]^-$:[65]

$$3IF_5+4O_2[AuF_6]=3[IF_6][AuF_6]+4O_2+AuF_3 \ .$$

VI. APPLICATIONS

The cation halogen compounds have a multiplicity of novel physical and chemical properties which lead to a wide variety of possibilities in their practical use. In the first place, being strong oxidants, they have been recommended as components of rocket fuels and in the technology of the processing of nuclear materials.[9]

The compounds $[Cl(ClF)][AsF_6]$, $[ClF_4][SbF_6]$, and $[BrF_2][SbF_6]$ proved to be excellent fluorinating agents at comparatively low temperatures in closed reactors and at low pressures developed in the process;[122,141,150,162] $[BrF_6].[AsF_6]$ is more effective than F_2 under the usual conditions, oxidising, for example Xe and O_2:

$$[BrF_6][AsF_6]+Xe=(XeF)\ [AsF_6]+BrF_5 \ ,$$

$$[BrF_6][AsF_6]+O_2=O_2[AsF_6]+BrF_5+0.5F_2 \ .$$

The effectiveness of the halogen cation compounds in organic synthesis has been mentioned frequently.[202,203] In particular, it is technologically convenient to synthesise fluorinated aromatic derivatives of iodine(VII) with the aid of $[IF_4][SbF_6]$.[203] The authors believe[203] that the halogen cation compounds lead to new possibilities for the synthesis of compounds containing Ar–Hal (Hal = I, Br, or Cl). The halogen cation compounds $[Cl(ClF)][AsF_6]$, $[ClF_2][AsF_6]$, $[ClF_4][SbF_6]$, and similar compounds can be used as solid sources of chlorine fluorides and devices for their storage. When necessary, these fluorides can be regenerated in a pure form.[141]

The most promising application of the halogen cation compounds is the synthesis of new substances by mixing solutions containing the corresponding halogen cation compound (Lewis acid) and the halogenate anion (Lewis base). The solvent in this instance is the interhalogen compound whose autoionisation leads to the formation of the cation and anion of the reactant. An example is provided by the reaction

$$[BrF_2][PF_6]+Ag[BrF_4]=Ag[PF_6]+2BrF_3 \ .$$

Numerous complexes, whose synthesis had been regarded as impossible previously, have been obtained by this method.[12,113,115,155,156,160,162,163] The reversibility of some of the reactions and the solvolysis of the product are complications in **synthesis** of this kind.

The exchange reactions involving the complex cations may be used for synthesis:[12,204]

$$[BrF_2][AuF_4]+SeF_4=(SeF_3)[AuF_4]+BrF_3 \ .$$

These reactions can be employed also for the purification of chemical fluorides.[205]

The determination of chemically combined oxygen in minerals, raw materials (ores), and metal oxides and phosphates is a difficult analytical problem whose solution has become possible after the appearance of the halogen cation compounds. In particular, when thermostable oxides (ThO_2, Al_2O_3, ZrO_2, etc.) and phosphates are heated with $[BrF_2][SbF_6]$ to temperatures above 330 °C, oxygen is evolved quantitatively.[12,122] The same reagent has been proposed[206] for the direct quantitative determination of chemically combined oxygen in alcohols and aliphatic and aromatic acids.

The reaction

$$Rn+[IF_6][SbF_6]=(RnF)[SbF_6]+IF_5$$

has been recommended[66,207] for the separation of a mixture of Rn, Xe, and Kr, for the determination of Rn in air, and for the removal of the radioactive radon impurity in air. The use of halogen cation compounds makes it possible to eliminate radon and other carcinogenic substances (^{218}Po, ^{214}Po, ^{214}Pb, and ^{214}Bi) almost completely from air in uranium mines.[207] The xenon evolved on dissolution of spent radioactive fuel may be utilised by means of reactions involving the formation of the adducts $2IF_5.XeF_2$ [208,209] and $IF_5.XeF_4$.[210,211]

VII. CONCLUSIONS

It follows from the data presented above that, in the direct synthesis of halogen cation compounds with halide ligands, halogens and diatomic interhalogen compounds should be used only together with powerful oxidants. Otherwise molecular ligands appear in the inner sphere with the complex-forming agent in the +1 oxidation state, for example, $[I(I_2)_2]^+$ and $[I(ICl)_2]^+$.[212–214] The halogen cation compounds with the cations $[ICl_4]^+$ and $[IBr_4]^+$ have not so far been obtained owing to the extreme instability of ICl_5 and IBr_5.[215]

The halogen cation compounds examined in this review are not distinguished by a wide variety of anions. The anions are mainly $[AsF_6]^-$, $[SbF_6]^-$, $[SbCl_6]^-$, $[BF_4]^-$, $[AlCl_4]^-$, and a few others. The properties of powerful halide ion acceptors can also be manifested by the fluorides and chlorides of elements capable of being converted into acido-complexes.

The dependence of the stability of the halogen cation compounds on the nature of the anions has not so far been accounted for. For example, BF_3 exhibits an appreciable accepting capacity in relation to fluoride ions, but it does not interact with either ClF_5 or with BrF_5 to form the cations $[ClF_4]^+$ and $[BrF_4]^+$.[188] The most stable halogen cation compounds contain almost always the anion $[AsF_6]^-$. The appearance in the anion of bromide or iodide ligands, which are readily oxidised, precludes the synthesis of the halogen cation compounds. Such ligands destabilise the cations, reconverting them into halogens or interhalogen compounds.

The more exothermic the formation reactions of anions of the type,

$$SbF_5+F^-\rightleftharpoons[SbF_6]^-,$$

the more stable should apparently be the resulting halogen cation compounds. Thus their stabilisation is also promoted by the electrolytic dissociation of interhalogen compounds[213] and by the ready solubility of the latter in Lewis acids functioning as halide ion acceptors. It has been established that the energy of abstraction of fluoride ions from halogen fluorides diminishes from ClF_5 to IF_5. The stability of the halogen cations associated with the same anion increases in the same direction:

$$[ClF_4]^+ < [BrF_4]^+ < [IF_4]^+.$$

The interaction of halogen fluorides and Lewis acids in the liquid phase is as a rule rapid and proceeds with a high yield.

Little is known about the mechanism of the formation reactions of the halogen cation compounds. The conditions governing the equilibria in solutions between the ions $[I_2]^+$ and $[I_3]^+$ and between $[I_3]^+$ and $[I_4]^{2+}$ or the causes preventing the appearance of the cations $[I_5]^+$ in the system I_2–$S_2O_6F_2$ or the cation $[I_3]^+$ in the system I_2–$AlCl_3$–NaCl [214] and favouring their formation in the system I_2–ICl–$AlCl_3$ have not been elucidated. The possibility of reactions of the type

$$3ICl \rightleftharpoons [I(ICl)]^+ + [ICl_2]^- \text{ or } 3ClF \rightleftharpoons [Cl(ClF)]^+ + [ClF_2]^-$$

is open to doubt. The dismutation

$$3ClF \rightleftharpoons ClF_3 + Cl_2 \text{ or } 3ICl \rightleftharpoons ICl_3 + I_2$$

followed by other reactions is more likely. It may be that in this process one of the stages involves an elimination reaction with formation of radicals. The appearance of the latter, for example $Cl_3^{\cdot}$, $ClF_2^{\cdot}$, [212] or $Cl_4^{\overset{+}{\cdot}}$, [120] has been frequently mentioned.

A fundamentally new method of synthesis of halogen cation compounds is that involving the explosive interaction between two different halides of the same metal. Single crystals of $[ClF_6][CuF_4]$, for example, have been obtained by this method from a mixture of CuF_2 and $CuCl_2$. [216]

In conclusion, it should be noted that the study of the chemistry of the halogen cation compounds is only just beginning and much still remains to be done before it occupies its due place in modern inorganic chemistry.

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Reactions of Unsaturated Systems with Hexavalent Chromium

Sh.O.Badanyan, T.T.Minasyan, and S.K.Vardapetyan

The literature data on the interaction of unsaturated compounds with hexavalent chromium reagents are surveyed. Attention is concentrated on reactions with coordination complexes of hexavalent chromium and also methods suitable for the chemospecific, regiospecific, and stereospecific oxidative generation of functional groups in highly unsaturated systems. The advances in the application of chromium(VI) in the synthesis of natural structures are described.

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I. INTRODUCTION

The oxo-derivatives of manganese, chromium, ruthenium, and osmium have been applied to an increasing extent in recent times for the generation of functional groups in organic molecules. Among the selectively acting oxo-derivatives of variable-valence metals, chromium compounds play the most important role, because the oxidative reactions based on them can be readily carried out and the reagents themselves are readily available and cheap. The oxidation of carbon–carbon multiple bonds by chromium(VI)–containing reagents leads to the formation of epoxides, glycols, aldehydes, ketones, and carboxylic acids.[1-9] Furthermore, if we add to this that coordination complexes of chromium can be used successfully for the conversion of hydroxy into the carbonyl groups in unsaturated systems, the prospects for their application in the chemistry of unsaturated compounds become evident.[10-19] For these purposes, one uses chromic acid (in water or in acetic or sulphuric acids), the dichromate ion (in water or in acetic acid), chromyl acetate (in acetic anhydride or in its mixture with acetic acid), t-butyl chromate, chromyl nitrate, coordination complexes of chromium dioxide, and chromyl chloride (in inert solvents).

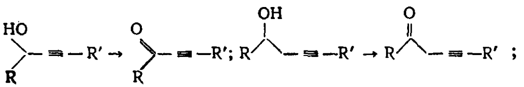
The literature data on the application of chromium compounds as oxidising agents for organic substrates available in foreign literature have been partly considered and surveyed.[20-27] Despite the enormous importance of the above reagents, there have been no Soviet reviews, which led us to compile and arrange systematically the data on the interaction of hexavalent chromium compounds with unsaturated compounds. The reactions of chromium derivatives with unsaturated systems can be arbitrarily divided into the following groups: (1) oxidation of hydroxy-groups and other functional groups; (2) oxidation of multiple bonds; (3) allylic oxidation.

II. REACTIONS OF UNSATURATED ALCOHOLS

The search for readily available and selectively active reagents for the oxidation of alcohols to carbonyl compounds has been for a long time the object of numerous investigations. An enormous number of reagents containing chromium(VI) were tested but the majority of them did not exhibit an adequate activity and selectivity and as a result proved to be unsuitable for use in modern organic synthesis.[28] However, the series of reagents considered in this review had been used successfully in reactions with unsaturated alcohols.

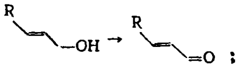
1. Oxidation by Chromic Acid, the Dichromate Ion, and t-Butyl Chromate

Chromic acid (H_2CrO_4) was first used as an oxidant in the conversion of derivatives of cyclopentenol into cyclopentenones and it was recommended that the reaction be carried out in acetic acid (Fieser's reagent) or in sulphuric acid.[29,30] A major advance in the oxidation of the hydroxy-group to the carbonyl group in unsaturated alcohols and in particular in acetylenic systems by chromium trioxide in sulphuric acid has been the successful employment of acetone as the solvent (Jones' reagent), which ensured high yields of carbonyl compounds:[31-38]



R = alkyl, aryl; R' = H, alkyl.

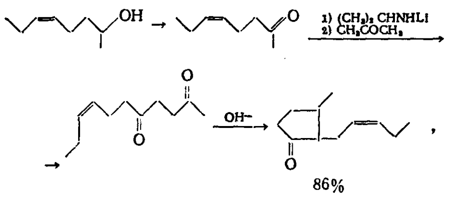
It has been reported that various primary allyl alcohols give rise to aldehydes in moderate yields on oxidation by the chromate ion in sulphuric acid:[39-43]



R = alkyl, alkenyl.

According to the results of a number of investigators,[30,31,44-48] when concentrated sulphuric acid is used, reactions with unsaturated primary alcohols do not stop at the aldehyde formation stage but continue until the formation of the corresponding acid. This fact has been used in the synthesis of the pheromone of the black carpet beetle—megatomoic acid.[47]

Other literature data exists concerning the oxidation of unsaturated alcohols to aldehydes with the aid of the Jones reagent.[49-51] Among them the use of chromic acid in the synthesis of *cis*-jasmone, in accordance with the scheme[52]



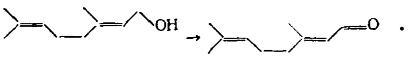
is of great interest.

The synthesis of a series of α-acetylenic carbonyl compounds is also of interest.[53–60]

The above methods have been used successfully in the conversion of polycyclic unsaturated carbinols into ketones.[61–64]

The dichromate ion $[Cr_2O_7]^{2-}$ in acetic or sulphuric acid has been used to oxidise various allyl alcohols.[65] The above reagent has been used successfully also to convert cholesterol into cholestanone[66] and also for the oxidation of propargyl alcohols.[67]

t-Butyl chromate ($t\text{-}Bu_2CrO_4$) has been used on a comparatively wide scale for the oxidation of the hydroxy-group in unsaturated systems, which demonstrates its advantage over other reagents. Studies in this field have been examined and surveyed by Matsuura and Suga.[68] Chromium trioxide in t-butyl alcohol was first used as the reagent for the oxidation of hydroxy-groups in unsaturated alcohols in the conversion of geraniol into geranial in 85% yield:[69]



Subsequently this reagent was applied successfully for the conversion of various allyl alcohols into unsaturated carbonyl compounds[70–72] and also for the oxidation of octa-3,5-diene-2,7-diol into the corresponding diketone.[73]

In the 1970's oxidising agents based on chromium trioxide began to be used in the presence of carriers. When chromium trioxide is added to a solution of an alcohol in a 1:3 mixture of diethyl ether with dichloromethane in the presence of celite, carbonyl compounds are formed.[74] There are data concerning the oxidation of unsaturated alcohols by chromic acid deposited on a polymeric carrier[75] and adsorbed on silica gel,[76] by the graphite chelate of chromium trioxide,[77] by chromium trioxide in hexamethylphosphoramide[78–80] deposited on wood charcoal[81] or on a polymer,[82] and by the dichromate of polyvinylpyridine.[83]

The mechanism of the oxidation of alcohols on polymers of saturated compounds has been the subject of investigations by many workers. It follows from these studies that the rate of oxidation depends on the concentration of the acid ester of chromic acid;[84–97] this dependence and the isotope effect[98] show that the slow stage involves the rupture of a C—H bond at the carbon atom linked to the hydroxy-group. The fact that the reaction is faster in deuterium oxide than in water is no less important.[99] These data agree with the hypotheses of both one- and two-electron transfer in the rate-limiting stage. According to Watanabe and Westheimer,[100] these two alternatives can be distinguished by employing the unusual ability of manganese(II) ions to induce the reaction. Thus, in the oxidation of isopropyl alcohol in the presence of a large excess of manganese(II) ions, half a mole of manganese dioxide is formed for each mole of acetone in accordance with the equations

$$(CH_3)_2CHOH + Cr^{VI} \rightarrow (CH_3)_2C{=}O + Cr^{IV} \;;$$
$$2Cr^{IV} + Mn^{II} \rightarrow MnO_2 + 2Cr^{III} \;.$$

In the absence of the alcohol, the reaction between hexavalent chromium and bivalent manganese does not take place. In the presence of a large excess of the alcohol, manganese(II) ions decrease the rate of oxidation by a factor of two:

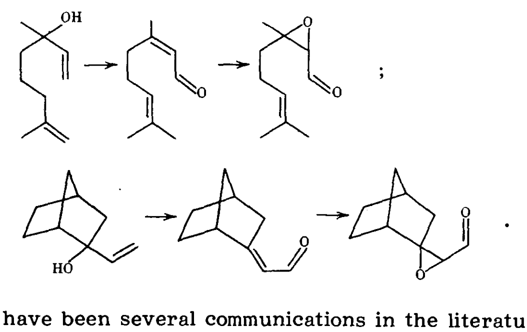
$$(CH_3)_2CHOH + Cr^{VI} \rightarrow (CH_3)_2C{=}O + Cr^{IV} \;;$$
$$Cr^{VI} + Cr^{VI} \rightarrow 2Cr^{V} \;;$$
$$2[Cr^{V} + (CH_3)_2CHOH \rightarrow (CH_3)_2C{=}O + Cr^{III}] \;.$$

It is seen from the equations presented that the oxidation is only one-third induced by hexavalent chromium and is two-thirds induced by quinquevalent chromium. The above examples of the induced oxidation demonstrate that chromium(IV) and chromium(V) complexes are formed as intermediates in the oxidation by chromium(VI). We may note that the latter are in fact effective oxidants which convert unsaturated alcohols into the corresponding carbonyl compounds.[101] In the rate-limiting stage, the intermediate chromic acid esters of primary and secondary alcohols are decomposed.[102,103] It has been suggested that the reaction proceeds via the formation of acid chromates,[104,105] which agrees best not only with the observed kinetics and the isotope effect but also with the presence of acid esters in the reaction medium.[106] Some workers assume that the reaction proceeds via the direct elimination of the hydride ion,[87,107,108] while others claim that chromic acid esters are formed initially.[103,109] However, despite the numerous data available,[82–86,105,110–123] it is difficult to make a final choice between the proposed mechanisms. Furthermore, since the rate of oxidation is independent of the oxidant concentration and corresponds to the rate of the acid-catalysed dehydration of alcohols to alkenes, some investigators have concluded that the initial stage involves the formation of an alkene, which is then oxidised by chromic acid.[124–126]

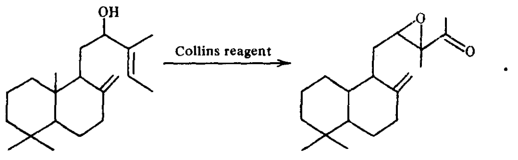
2. Oxidation by Coordination Complexes of Chromium Trioxide

First Sarett and co-workers[127] and then Collins et al.[128] demonstrated that the complex of chromium trioxide with pyridine[129] can be used successfully for the oxidation of alcohols to carbonyl compounds. Subsequently pyridine chromate (PC) ($C_5H_5.CrO_3$), the reagent of Sarett and Collins, was used to oxidise allyl and benzyl alcohols[130–131] — geraniol, nerol, citronellol, and cinnamyl alcohol[131] and bicyclic and tricyclic unsaturated carbinols,[132,133] including cholesterol[134] and cholesteryl acetate,[135] also in the synthesis of prostaglandins.[136]

The oxidation of tertiary and secondary allyl alcohols by the Collins reagent involves an oxidative rearrangement with formation of αβ-unsaturated aldehydes.[16] Under the reaction conditions, the latter are mainly converted into epoxy-derivatives:



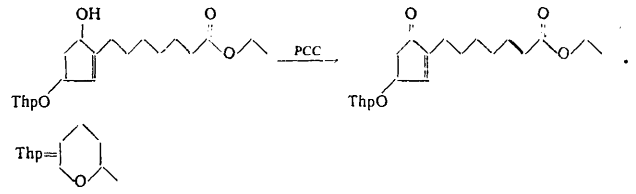
There have been several communications in the literature about the formation of epoxy-derivatives as a result of oxidation by other chromium reagents,[137–146] but none has been synthetically useful. In this sense the example presented below is valuable in biogenetic syntheses:[16]



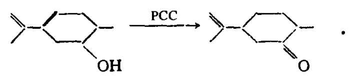
However, following the publication of the interesting report by Corey and Suggs,[10] who proposed pyridinium chlorochromate (PCC) $\{C_5H_5\overset{+}{N}H[CrO_3Cl]^-\}$ as a safe and readily available reagent, PC began to be used to a lesser extent.

In contrast to the Sarett and Collins oxidant, the Corey complex is non-hygroscopic, is safe, and there is no need to employ it in a fivefold and sixfold excess.[10,147] Hitherto, the Corey reagent has been used in somewhat modified forms; it is employed in a buffer mixture,[10] and in the forms where it is deposited on celite,[148] alumina,[149] poly(vinyl alcohol),[150] and molecular sieves.[151]

The Corey reagent is an effective oxidant for the conversion of many allyl[10,149,150] and homoallyl[151,152] alcohols into the corresponding carbonyl compound. With its aid, citronellal can be obtained in satisfactory yields from citronellol.[10,149] The reaction of a hydroxyacid ester presented below is of interest:[153]

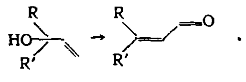


Isopulegone can be obtained in a quantitative yield in accordance with the following scheme:[149]



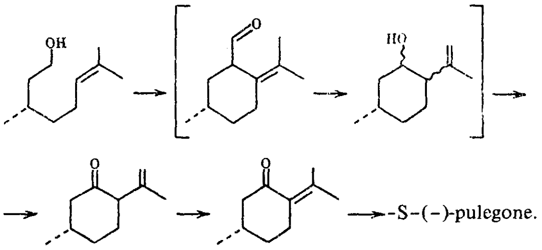
When alkenyl alcohols with a specific configuration of the double bond are oxidised, *cis–trans* isomerisation is observed.[10] In steroids containing several hydroxy-groups, including some of the allyl type, it is possible to oxidise the required hydroxy-group by varying the conditions.[154–157]

On interaction with PCC, tertiary and certain secondary allyl alcohols undergo an oxidative rearrangement, forming exclusively an unsaturated aldehyde and ketones in almost quantitative yields:[15,16,158]



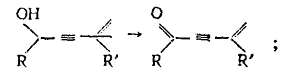
Such oxidation with a rearrangement is caused, according to the authors, by the weakly acid character of PCC, under the influence of which tertiary alcohols rearrange to primary alcohols and the oxidation of the latter leads to unsaturated aldehydes.[16,158]

Another promising synthetic application of the Corey reagent is in the oxidative cyclisation of unsaturated alcohols. Thus (–)-citronellol can be readily converted into (–)-pulegol by treatment with PCC:[13]



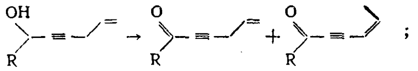
The acid properties of PCC, which induces the annelation of a number of other linear and cyclic unsaturated alcohols or aldehydes to form cyclohexanone derivatives, also promote this course of the reaction.[14] The above reaction is suitable for the asymmetric synthesis of prostaglandins.[159,160]

Pyridine chlorochromate has been used successfully also for the oxidation of certain propargyl alcohols;[10,161,162] it is exceptionally suitable for the synthesis of vinylacetylenic aldehydes and ketones:[163–165]



R = H, alkyl, aryl; R′ = H, CH₃.

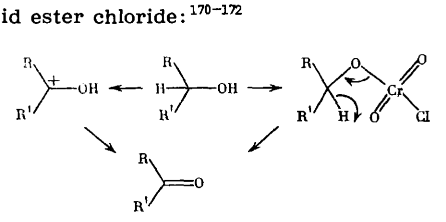
It is noteworthy that reactions of primary and secondary allylacetylenic carbinols with PCC are accompanied by a prototropic rearrangement with formation of mixtures of allyl- and propenyl-propargyl aldehydes and ketones:[166]



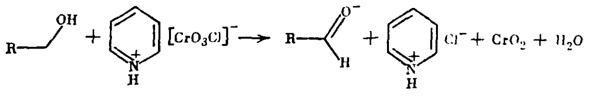
R = H, alkyl.

This reagent has also been used successfully for the oxidation of propenyl-acetylenic[166] and vinylallenic alcohols,[166] for the synthesis of *cis*-tagetone[167] and ocimenone,[168] and for reactions in the series of gibberellins.[51] The oxidation of unsaturated alcohols to butanolide derivatives is also of interest.[169]

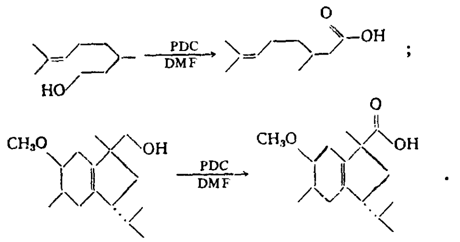
The mechanism of the oxidation of alcohols by pyridinium chlorochromate has been investigated by a number of workers.[170–177] Two main pathways whereby alcohols are converted into carbonyl compounds have been suggested: via the intermediate formation of the carbonium ion or via a chromic acid ester chloride:[170–172]



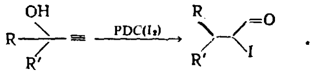
The authors believe that in both cases three electrons are transferred and that the oxidation state of chromium changes from +6 to +3 during the reaction. However, it has been noted that[177] two electrons are transferred in the above reaction in accordance with the mechanism



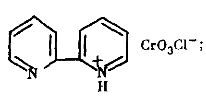
Pyridinium dichromate (PDC) $(C_5H_5\overset{+}{N}H)_2Cr_2O_7^{2-}$ in dimethylformamide (DMF) was suggested in 1979 as the oxidant for the selective conversion of the hydroxy-group into the carbonyl group.[12] The reagent oxidises rapidly 2-cyclohexanol, cinnamyl alcohol, and geraniol to 2-cyclohexenone, cinnamaldehyde, and geranial respectively in quantitative yields. In many instances the formation of the corresponding acids from the alcohols has been observed, for example:



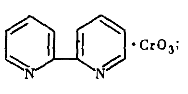
PDC in methylene chloride proved to be an even milder oxidant.[12] Regardless of the nature of the substrate, the reaction proceeds in this instance only as far as the formation of aldehydes. For example, citronellol gives rise to citronellal in 92% yield. It has also been noted that allyl alcohols are oxidised faster than their saturated analogues (2-cyclohexenol 10 times faster than cyclohexanol). Pyridinium dichromate in methylene chloride has been used to synthesise a series of αβ-unsaturated carbonyl compounds containing both double and triple bonds. Here it is noteworthy that the oxidation of geraniol to geranial involves partial inversion (9%). This *E*/*Z* isomerisation takes place before oxidation to geranial in the stage involving the formation of the intermediate chromate ester as a consequence of a reversible allyl rearrangement. PDC has been used successfully in the syntheses of pheromones.[178,179] In the presence of iodine in methylene chloride, this reagent converts smoothly tertiary acetylenic carbinols into αβ-unsaturated α-iodoaldehydes:[180]



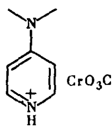
2,2′-Bipyridyl chlorochromate (BPCC) and the corresponding chromate (BPC)[181–183] as well as 4-(dimethylamino)pyridinium chlorochromate (DMAPCC),[184,185] have been proposed as oxidants for the oxidation of the hydroxy-group to the carbonyl group:



BPCC

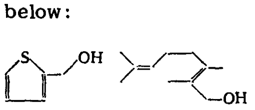


BPC

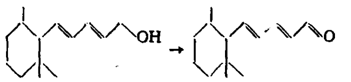


DMAPCC

2,2′-Bipyridyl chlorochromate containing an internal buffer (the 2,2′-bipyridyl system) has been recommended for the oxidation of alcohols containing acid-sensitive groups, of the type presented below:



As regards BPC, one should note, on the one hand, certain difficulties in its use, which are also characteristic of the Collins reagent (increase of the reaction time and the necessity to use an appreciable excess of the reagent and, on the other hand, the special selectivity in the oxidation of allyl and benzyl alcohols). The authors note that DMAPCC combines the selectivity of BPC and the advantages of BPCC. DMAPCC has been used successfully for the selective oxidation of polyols.[184] This reagent converts geraniol into geranial in a quantitative yield. The oxidation of the exceptionally sensitive vitamin A synthone into the corresponding aldehyde also proceeds smoothly:[184]



However, when DMAPCC is used in certain cases, the complete inversion of the configuration of the initial *Z*-alcohols is observed together with oxidation, and *E*-aldehydes are obtained.[184] Despite its limited applicability compared with its chlorine analogue, pyridinium fluorochromate has a less pronounced acidity and is an effective agent for the oxidation of a number of polycyclic organic substrates.[186–188]

Ammonium dichromate $(NH_4)_2Cr_2O_7$, which has been used to convert primary allyl alcohols, including geraniol and nerol, into aldehydes, manifested oxidising properties.[131] Among nitrogen complexes of chromium trioxide, mention should also be made of naphthyridinium chlorochromate $(C_8H_6\overset{+}{N}_2H.CrO_3Cl^-)$,[189] pyrazinium chlorochromate $(C_4H_4.\overset{+}{N}_2H.CrO_3Cl^-)$,[189] tetrabutylammonium chlorochromate $(Bu_4\overset{+}{N}.CrO_3Cl^-)$,[190] dimethylpyrazole chromate $(C_5H_8N_2.CrO_3)$,[16,191,192] tetrabutylammonium dichromate $(Bu_4\overset{+}{N}_2Cr_2.O_7^{2-})$,[193] the pyridine complex of oxodiperoxochromium $(C_5H_5N.CrO_5)$,[194] and the dipyridine complex of chromium trioxide $(2C_5H_5N.CrO_3)$ in acetic acid.[195] Poly(4-vinylpyridinium dichromate) (PVPDC) $P-C{=}CHCH{=}NH(Cr_2.O_7)_{0.5}CH{=}CH_2$—the polymeric analogue of pyridinium chlorochromate—has been proposed recently.[196] It has been noted that the main advantage of the polymeric reagent is the ease of the purification of the final product, because both the initial polymer, used in excess to complete the reaction, and the reaction product are insoluble in the reaction medium and can be removed by simple filtration.

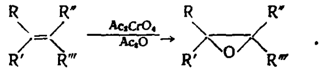
III. REACTIONS OF CARBON–CARBON MULTIPLE BONDS

There are literature data on the oxidation of double bonds both with decomposition of the unsaturated systems and without change in the carbon chain. The latter are of great interest and will be the subject of further discussion.

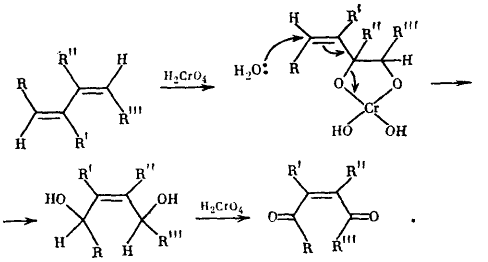
1. Oxidation by Chromic Acid, Chromyl Acetate, and Chromyl Nitrate

The oxidation of tetraphenylethylene by chromium trioxide (CrO_3) in acetic acid leads to an epoxide.[9,197,198] Alkenes of various types have been introduced into the reaction but mainly allylic oxidation was observed under these conditions.[199–213] The reactions of alkenes in aqueous acid media usually lead to products of the rearrangement of the epoxides formed initially.[2,5,6,214–218] Furthermore, on treatment with acid, camphene oxide affords camphenaldehyde, while the reaction of camphene with chromic acid leads to camphor and not to camphenic acid.[7] Assuming that the acid-catalysed rearrangement of camphene hydrate to isoborneol is faster than the oxidation of camphene, the authors conclude that camphor is obtained by the oxidation of isoborneol. In contrast to this, the reaction of 1,1-diarylethylenes with chromic acid affords only the cleavage product but not the epoxides, which were shown to be unreactive under the conditions used.[219,220] It has therefore been suggested that epoxides cannot be intermediates in the oxidation of the multiple bonds by chromic acid. It is also of interest that the very electrophilic addition of chromic acid is disproved by the fact that the carbonium ion formed in this process should have given rise to a large amount of a rearranged product.[221,222]

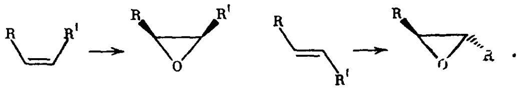
The reactions of alkenes with chromyl acetate (Ac_2CrO_4) proceed more successfully. They have been studied in detail in a number of investigations.[1,3,4,192,219,220] Here the main products of the interaction are epoxides, whose yield is higher the greater the degree of substitution at the double bond:



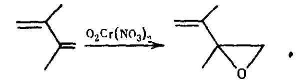
It is noteworthy that both the products of the rearrangement of the postulated epoxides[3,4,6,223–225] and acetates[226] and pinacol carbonates[8] are then isolated. Conjugated dienes also react successfully with chromic acid, which leads to the formation of enediones:[206–208,227]



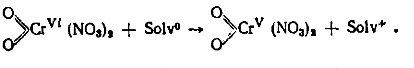
Chromyl nitrate $O_2Cr(NO_3)_2$ has been proposed recently as a reagent for the epoxidation of olefins.[228] It has been shown that different alkenes react stereospecifically at −78 °C in aprotic media (pyridine, DMF, or methylene chloride) with chromyl nitrate to form epoxides:



A high degree of retention of configuration has also been observed in the oxidation of olefins by chromyl acetate.[229,230] The products of the oxidation in acetone were ketals.[228] 2,3-Dimethylbutadiene enters smoothly into this reaction:



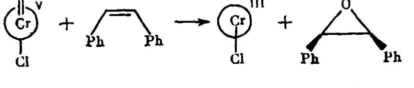
The authors believe that oxochromium(V), formed from chromium(VI) as a result of the preliminary one-electron oxidation of the solvent (Solv), is the active species in epoxidation by chromyl nitrate:[228]



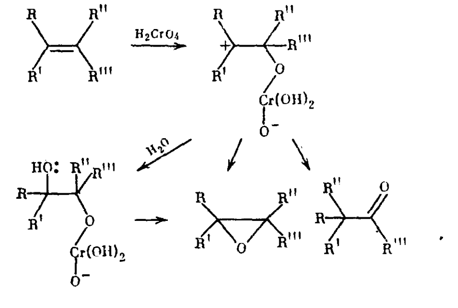
$$O_2Cr^{VI}(NO_3)_2 + Solv^0 \rightarrow O_2Cr^{V}(NO_3)_2 + Solv^+ .$$

The reaction then proceeds in accordance with the equation

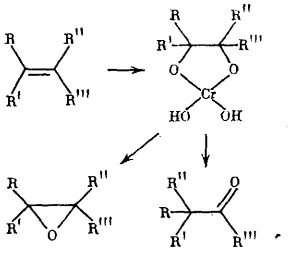
The active involvement of the intermediate chromium(V) has been confirmed by comparison with the ability of "macrocyclic oxochromium(V)" to convert alkenes effectively with a high degree of stereospecificity:[231]



The corresponding intermediates have been detected by EPR.[229] Despite the inadequacy of data concerning the role of chromium(IV) and chromium(V), the influence of substituents and stoichiometry, etc., it is believed that electrophilic attack on the double bond takes place:[219,220,232,233]



Cycloaddition, by analogy with oxidation by permanganate, is not ruled out either:[221,222]



The non-stereospecific epoxidation of tetraarylethylenes by chromyl acetate indicates indirectly that the reaction proceeds via a carbonium ion, in contrast to the oxidation of alkenes by permanganate,[234–236] where process stereospecificity is observed. The hypothesis of the intermediate formation of carbonium ions in the oxidation of alkenes by chromium trioxide in acetic anhydride to oxirans has been developed in other investigations.[219,220,237,238] These conditions ensure satisfactory yields of oxirans, while in the presence of hydrogen in the allyl position, the competing allylic oxidation is observed.[239]

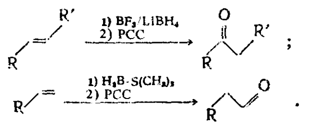
Kinetic data have shown that the rate of oxidation by chromic acid increases with increase of the degree of branching of the olefin chain. It has been established that the rate depends on the number of alkyl substituents to a greater extent than on the configuration of the olefin.[240] The acceleration of the reaction by the substituent at the double bond has also been noted in the oxidation of chalcones (phenyl styryl ketones); it was shown that electron-donating groups in the *para*-position in the benzene ring increase the rate, while electron-accepting groups diminish it.[241] In terms of their influence on the activity, the groups can be arranged in a sequence indicating the electrophilic character of the process:

$$4\text{-}OCH_3 > 3\text{-}OCH_3 > 2\text{-}OCH_3 > 4\text{-}Cl > 3\text{-}Cl > H > 3\text{-}NO_2 > 4\text{-}NO_2 .$$

The reaction is thought to proceed via a three-membered cyclic activated complex.[241,242] Analogous complexes have been postulated in the oxidation of alkenes by chromyl chloride.[243,244]

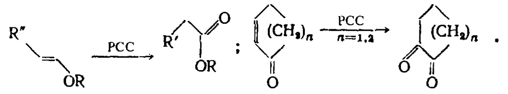
2. Oxidation by Coordination Complexes of Chromium Trioxide

The oxidation of multiple bonds by chromium trioxide complexes proceeds via the preliminary conversion of alkenes into organoelemental derivatives.[245–247] A promising variant involves their interaction with hydroborating agents and subsequent oxidation with PCC:[248,249]

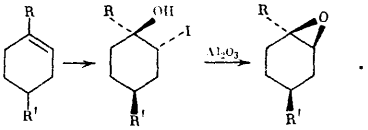


Numerous alkenes, including some with functional-group substituents, have been converted into aldehydes and ketones by this method.[250–252] A series of unsaturated carbonyl compounds have been synthesised in an analogous way via the dissociation of the C–Sn bond in organotin compounds by the pyridine complex of chromium trioxide.[253]

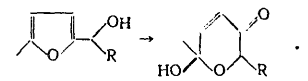
As already mentioned, direct oxidation of multiple bonds by pyridinium chlorochromate is difficult and, furthermore, its inertness with respect to double[10] and triple[10,254] bonds has been reported. Nevertheless, it has been established that vinyl ethers interact smoothly with PCC:[255]



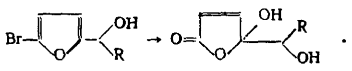
In the presence of iodine, trisubstituted olefins are converted by PDC regiospecifically and stereospecifically into iodohydrins and epoxides.[256] Certain natural polyenes, subjected to an analogous treatment, have been converted selectively into iodohydrins and then into epoxides:[256]



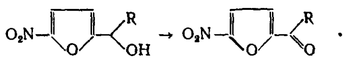
Substituted furans are also fairly sensitive to PCC:[257–261]



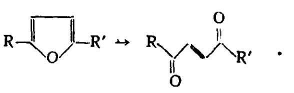
In the case of bromofurylcarbinol, ring expansion is not observed and the reaction leads to the formation of γ-hydroxybutenolides:[262–268]



Under analogous conditions, nitrofurylcarbinol is converted into a ketone:[269]

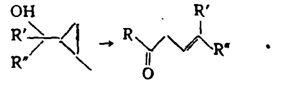


Among these reactions, the oxidative opening of the rings of arylfurans to form linear diketones is no less important:[270]



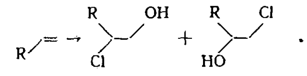
It is believed that the mechanism of the oxidation of furans by PCC includes the initial electrophilic 1,4-addition with subsequent ring opening.[270,272,273]

Ring opening has been observed also in the conversion of cyclopropylcarbinols into unsaturated ketones:[271]

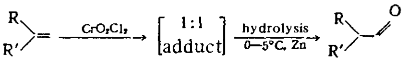


3. Oxidation by Chromyl Chloride

The oxidation of alkenes by chromyl chloride was already known at the beginning of the century.[274–281] However, the products thus obtained were first identified only in 1950.[282] It was found that the oxidation entails the preferential formation of chlorohydrins with a primary-hydroxy-group:[282,283]

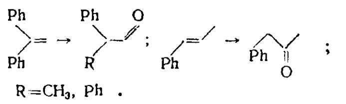


When cycyoalkenes are used in this reaction, mixtures of *cis*- and *trans*-chlorohydrins are formed. It is remarkable that the *trans*- and *cis*-isomers predominate respectively for cyclohexene and cyclopentene.[283] The formation of carbonyl compounds has also been noted under these conditions.[282,283] Other workers obtained mainly aldehydes from disubstituted terminal olefins;[279] the reaction involving phenylmethylethylene produces benzyl methyl ketone.[284] However, a more detailed study of the reaction[279, 282,283,285] showed that the reductive hydrolytic stage is mainly responsible for the reaction pathway and the yields of products. When zinc dust was used as the reductant instead of sulphur dioxide,[286] it was possible to obtain carbonyl compounds in high yields:[285]



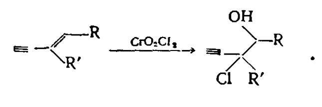
This reaction is of practical interest and has been used in the synthesis of chrysomelidial and gastrolactone.[287]

Among substituted olefins used in the reaction with chromyl chloride, styrenes are of great interest. A particular reason for this is that the familiar Etard reaction (oxidation of arylalkanes) proceeds according to many investigators via the intermediate formation of arylalkenes.[283, 286, 288–290] The interaction of chromyl chloride with *trans*-1-phenylpropene yielded at least seven compounds, including 1-phenyl-2-propanol.[288] However, other workers isolated only 1-phenyl-2-propanol.[284,291] Satisfactory results have been achieved in the oxidation of both 1,1- and 1,2-disubstituted styrenes (1-methyl-1-phenylethylene, 1,2-diphenylethylene, *trans*-1-phenyl-1-propene) by chromyl chloride at a low temperature where the reductive hydrolysis of the intermediate was carried out with the aid of zinc dust:[291]



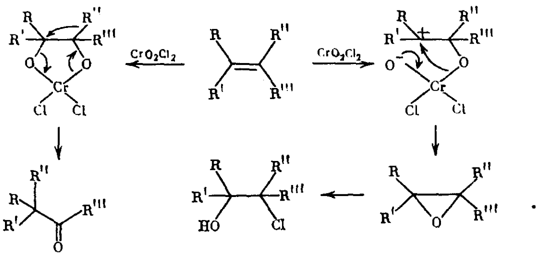
The oxidation of alkenes,[282,285,292] cycloalkenes,[284,293] and styrenes[291,293] by chromyl chloride has been the subject of controversy. It has been reported that treatment with an excess of chromyl chloride results in the formation of chlorohydrins in low yields,[282,292] while the reaction involving the use of equimolar ratios of the reactants produces carbonyl compounds.[243,285]

It has been established quite recently that various enynes interact selectively with chromyl chloride via the double bond with formation of alkyne chlorohydrins:[294]



A whole series of different enyne ethers, esters, and ketones have been introduced into this reaction.[294]

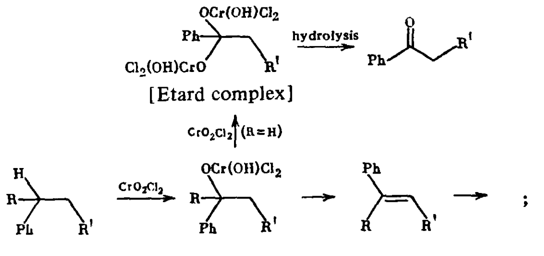
The interaction of chromyl chloride with multiple bonds is usually represented as proceeding via cyclic intermediates[282,283,291,295,296] in accordance with the scheme[243,285]

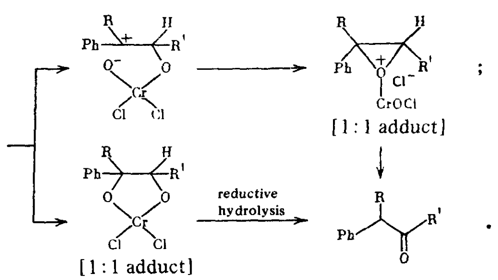


However, this hypothesis required confirmation with the aid of kinetic studies. Freeman and Yamachika[297] attempted to investigate the kinetics of the oxidation of cyclopentene, cyclohexene, and norbornene by chromyl chloride.[297]

The influence of ring size on the nature of the activated complex and on the rate of epoxidation,[298] oxidation with chromic acid,[240] and the addition of dibromocarbene and phenyl and picryl azides[299–301] had been investigated earlier. For example, in 1,3-dipolar cycloaddition reactions (via a five-membered cyclic activated complex), norbornene reacts 10^3—10^4 times faster than cyclohexene,[297] while the difference between the rates of epoxidation, addition of dibromocarbene to cyclopentene and cyclohexene or their epoxidation (which proceed via a three-membered ring) is very small.[299–301] Measurements of the rate constants for the oxidation of the above compounds by chromyl chloride and of the thermodynamic parameters under the conditions of a large excess of the cycloalkene and their comparison led the authors to the conclusion that the activated complexes in the case of cyclopentene and cyclohexene may be three- and five-membered cyclic compounds,[297] while in the case of norbornene only a five-membered transition state is produced. The same workers believe that, in the interaction of norbornene with chromyl chloride, an intermediate should be formed with a structure such that it can be converted into a *cis*-glycol or an epoxide rearrangement product.[242] However, it was soon established that, in the oxidation of norbornene and many of its substituted analogues at −80 °C, 74% of the isolated products are due to the initial formation of an *exo-cis*-chlorohydrin[302] and only 5% correspond to those predicted by Freeman. In contrast to the reaction of chromyl chloride with alkenes,[283] a mixture of *cis*- and *trans*-isomers is not formed in this instance—the interaction is stereospecific in the *exo*-position.[302]

In the early communications on the oxidation of styrene and its derivatives with chromyl chloride,[283,285,291,297,303,307] kinetic data were not quoted. However, styrenes[283] and cycloalkenes[296] were postulated as intermediates in the oxidation of cycloalkanes and arylalkanes respectively,[291,303,308] so that the overall process mechanism was represented as follows:



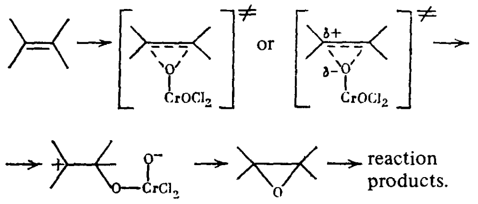


Subsequently, in the study of the kinetics of the reaction of chromyl chloride with styrenes, it was concluded[244] that it is of first order (first order with respect to each reactant) and that there is a correlation between the σ^+ constants of the substituents and the rate constants. These data as well as the thermodynamic parameters of the reaction agree with the mechanism involving electrophilic attack by chromyl chloride on the multiple bond with formation of resonance-stabilised partially bridged five-membered or three-membered activated complexes. From the value $\rho^+ = 1.99$, it was assumed in other investigations[309–312] that these complexes are hardly likely to be products of *cis*-addition, although this type of mechanism with an unbalanced charge in the transition state in cycloaddition has in fact been postulated.[313,314] However, since values of ρ^+ ranging from −3 to −5 were noted in reactions with a high degree of carbonium ion character of the transition state, the relatively low value $\rho^+ = -1.99$ conflicts with the idea that there is a full positive charge on the benzyl carbon.[244] Spectrophotometric data for the interaction of alkenes with chromyl chloride agree best with the idea that a three-membered cyclic intermediate complex is formed in the rate-determining stage.[243,291] The data obtained in the oxidation of bicyclic systems suggested that here too three-membered cyclic transition states are produced.[291] Next, the study of the kinetics of the addition of chromyl chloride to substituted styrenes showed that the rate of reaction increases after the introduction of electron-donating substituents. α-Methylstyrene is more reactive than *cis*-β-methylstyrene. The latter is oxidised at a lower rate than *trans*-β-methylstyrene, while *cis*-stilbene reacts twice as fast as *trans*-stilbene and 1,1-diphenylethylene is almost twice as reactive as α-methylstyrene and is superior to styrene by a factor of 13.[242] However, the question of the relative reactivities of the *cis*- and *trans*-isomers is not always susceptible to interpretations; for example, the higher reactivity of *cis*-stilbene compared with *trans*-stilbene has been observed in bromination reactions[315–317] and in oxidation with peracetic acid.[318,319] In contrast to this, *trans*-stilbene reacts faster than the *cis*-isomer in oxidation with chromic acid[240] and in *cis*-1,3-dipolar cycloaddition.[320] It is also essential to emphasise that neither *cis*- nor *trans*-stilbene afforded the expected carbonyl product on oxidation with chromyl chloride under the experimental conditions employed[285,291,321,322] and that they were successfully oxidised by chromyl chloride to carbonyl compounds only by varying the conditions.[323]

In the study of the kinetics of the oxidation of a number of alkenes, the first order of the reaction with respect to each reactant was observed.[243] The reaction is little influenced by steric factors and is characterised by low enthalpies of activation ($\Delta H^{\neq} = 5.4-7.2$ kcal mol^{-1}) and high negative entropies of activation ($\Delta S^{\neq} = -27.4 - -40.7$). Excellent correlations have been obtained between the rate constants and Taft σ^+ constants as well as a good correlation based on the Hammett equation.[243] Comparison of the relative reactivities in the oxidation with chromyl chloride and in other electrophilic reactions of alkenes (the addition of bromine and chlorine, oxidation with chromic acid, and epoxidation) suggested that the rate limiting stage involves a partially positively charged three-membered activated complex like the activated complex in the epoxidation of alkenes by peracids[324] or in the oxidation of alkenes with chromic acid.[240] From these data, the authors rule out the concerted *cis*-1,3-dipolar addition of chromyl chloride to the multiple bond in the rate determining stage, since this does not agree with kinetic data obtained for ring- or chain-substituted styrenes.[244,282] On this basis,[243] using the principle of the relative reactivities in solvolytic reactions,[325] oxidation with chromic acid,[239] epoxidation,[298,324] chlorination,[326] bromination,[327] and the addition of carbenes,[290,328] Freeman et al.[243] elucidated the nature of the activated complex in the oxidation of alkenes with chromyl chloride. The relative reactivities of alkenes in relation to chromyl chloride were obtained:[243]

pent-1-ene	1.22	2,3,3-trimethylbut-1-ene	**10.5**
hex-1-ene	1.00	2,4,4-trimethylpent-1-ene	**23.6**
oct-1-ene	0.77	*cis*-pent-2-ene	**14.8**
dec-1-ene	0.88	*trans*-pent-2-ene	**15.1**
2-methylpent-1-ene	8.00	2-methylbut-2-ene	**202.0**
3,3-dimethylbut-1-ene	5.36	2,3-dimethylbut-2-ene	**3910**
4,4-dimethyl-2-neopentylpent-1-ene	7.54	2,4,4-trimethylpent-2-ene	**1380**
cyclopentene	4.9	norbornene	**312**
cyclohexene	1.0	styrene	**366**

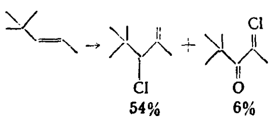
It is noteworthy that the mechanism of the oxidation of single and multiple carbon—carbon bonds with chromyl chloride still remains controversial.[292,293,304,305,329–335] Nevertheless, for the intermediate complex the rate of formation of which determines the rate of the entire reaction, a three-membered structure was adopted in the case of alkenes[282,293,296,297,329] and three- and five-membered asymmetric structures in the case of styrenes.[242,244,335] In an attempt to elucidate further the nature of the oxidation of cycloalkenes by chromyl chloride,[335] the kinetic data and thermodynamic parameters obtained were compared with data for the rearrangement of the epoxides;[218,219,242,334,336,337] the authors concluded that the process proceeds via the formation of epoxides, but the possibility of the intermediate formation of a carbonium ion was not ruled out:



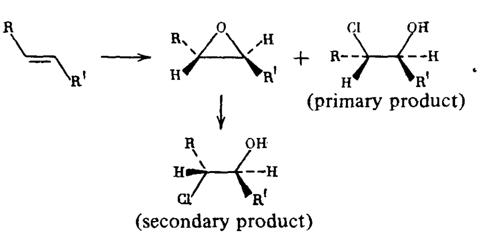
In their view, the fact that the rate of oxidation increases with increase of the number of methyl groups at the double bond agrees with the hypothesis. The involvement of a positively charged asymmetric three-membered activated complex in the rate limiting stage is indicated also by the fact that almost identical mixtures of final products are obtained from the following pairs of compounds in their reactions with chromyl chloride: 1-methylcyclopentene and methylenecyclopentane, 1-methylcyclohexene and methylene cyclohexane, and 1-methylenecycloheptene and methylenecycloheptane.[335]

The mechanism of the oxidation of multiple bonds has been formulated in a different way by Sharpless et al.,[230] who believe that reactions involving oxidation by metal oxo-compounds in general and by chromyl chloride in particular, begin with attack by the organic reductant on the metallic centre.[293] They believe that the mechanism proposed in a number of studies,[242,243,282,283,291,292,335,338,339] involving the formation of a three-membered intermediate, obtained by the electrophilic interaction of $[CrO_2Cl]^+$ with the olefin, followed by the attack on the latter from the rear by a chloride ion, is based on data showing that cyclohexene gives rise to *trans*-chlorohydrin, while the terminal olefins are products of the addition of the elements of the addend contrary to the Markovnikov rule. However, the authors note that this picture disagrees with the result of a study[283] where both *cis*- and *trans*-chlorohydrins were obtained from cyclohexene and cyclopentene. It was therefore necessary to assume that the reaction proceeds via a carbonium ion intermediate and that the latter is responsible for the formation of the *cis*- and *trans*-products.

It has been shown that the oxidation of *E*-t-butylmethylethylene with chromyl chloride in acetone results in the formation of mainly a ketone and the product of the Wagner—Meerwein rearrangement:[340]

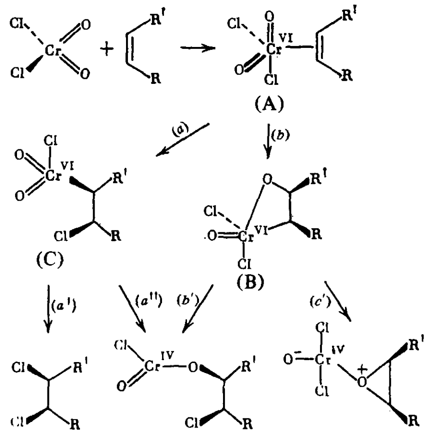


The authors believe that this result conflicts with the possibility of the existence of the intermediate structures presented above. On the other hand, it is known that the oxidation of olefins with chromyl chloride leads mainly to complex mixtures of compounds.[282,283,339] However, it has been reported recently[341,342] that epoxides are formed at a low temperature, although it has in fact been stated[302] that *exo*-*cis*-chlorohydrin is the main product in the reaction of chromyl chloride with norbornene. Sharpless et al. established unexpectedly that *cis*-addition is a common feature of the reactions of chromyl chloride with olefins.[230] On comparing the results of the oxidation of different alkenes with chromyl chloride at low temperatures and of the addition of the elements of HOCl to the same olefin, the authors concluded that the epoxides and chlorohydrin are the results of *cis*-addition and are the primary oxidation products, while the isomeric chlorohydrin (the product of *trans*-addition) is a secondary product obtained as a consequence of the opening of the epoxide ring:



It has been found that, analogously to other chromium reagents,[343] chromyl chloride is stereospecific and that epoxides with the geometry of the initial olefin are formed when it is used.

It has been shown[230] that the oxidation yields also a certain amount of dichloro-derivatives, which are likewise formed as a result of *cis*-addition. In their view, this can be in no way accounted for by the mechanisms proposed previously. On the basis of these data and also the fact that carbonyl compounds (aldehydes and ketones) give rise to nucleophilic reactions involving exclusively the carbon of the carbonyl group despite being less polarised than metal oxides, the authors assume that the oxidation of alkenes with chromyl chloride proceeds via the formation of organometallic intermediates:[230]



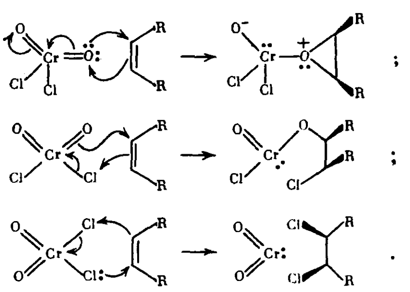
It has been suggested that the complex (A) is formed initially from the olefin and chromyl chloride. In the case of ligands more basic than olefins, stable type (A) complexes are known (chromium trioxide–bipyridyl, osmium tetroxide–pyridine). In a transition metal complex of type (A), the displacement of the coordinated olefin with formation of a metal-ligand either π- or σ-bond is a likely process. For this reason, the authors proposed two reaction pathways, (*a*) and (*b*), for chromyl chloride, which lead to organometallic intermediate complexes of chromium(VI). Via pathway (*a*), the olefin is inserted in the chromium–carbon bond (*cis*-chlorometallation), forming the alkylchromium intermediate complex (C), which is converted into the dichloride, pathway (*a*′), involves reductive elimination or [conversion?]† into the chromium derivative of chlorohydrin, and pathway (*a*″) involves migration of the alkyl group from chromium to oxygen. Both these processes take place with retention of the configuration of the carbon centre and result in *cis*-addition. Reductive elimination with formation of a chlorine–carbon bond (pathway *a*′) is well known in organic chemistry and takes place with retention of the configuration at the carbon atom.[344–346] The migration of 1,2-shift via pathway (*b*′) can take place, by analogy with the Stevens rearrangement, only with retention of the configuration at the carbon atom.[347] The earlier hypothesis of high-valence organometallic compounds such as the compounds (A), (B), and (C) would seem to be unrealistic. However, the literature, starting from as early as 1970's has been saturated by examples of organometallic derivatives of vanadium,[348,349] tantalum,[350] chromium,[351,352] tungsten,[353] and rhenium.[354,355] A tungsten complex (CH_3WO_2Cl), whose structure is very similar to that of organometallic type (C) intermediates, has been isolated and characterised.[353]

The mechanism presented actually involves [2 + 2] addition. The competing pathways (*a*) and (*b*) are especially sensitive to the nature of the medium, as expected. When the reaction is carried out in acetone or in the presence of a nucleophile (the chloride ion), the yield of chlorides increases.[341,356] Next it was established that, in oxidation with chromyl chloride in the presence of lithium bromide, only bromohydrins and bromoketones are obtained, because the bromide ion is more nucleophilic than the chloride ion:

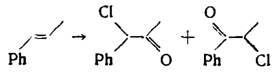
$$CrO_2Cl_2 \xrightarrow{2Br^-} CrO_2Br_2 + 2Cl^- \ .$$

The *cis*-addition of chromyl bromide leads to the final product.[230]

Sharpless and co-workers also did not rule out a mechanism involving direct attack on the heteroatom in accordance with the following schemes:



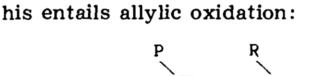
They had already established that different internal olefins can be converted into α-chlorohydrins by oxidation with chromyl chloride in acetone.[340] *cis*-Olefins react more slowly and with lower yields;[357] when the reaction mixture is treated with zinc dust, ketones are isolated.[340] In certain cases, for example with *E*-methylphenylethylene, a mixture of isomeric chloroketones in proportions of 3 : 1 is produced:



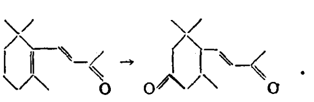
Thus new aspects of the oxidation of alkenes with chromyl chloride (via the initial formation of a high valence complex of the transition metal with a chromium–carbon σ-bond) have been examined and it has been shown that the primary oxidation products are epoxides and chlorohydrins.

IV. ALLYLIC OXIDATION

Treibs and Schmidt[358] showed for the first time that chromium trioxide in acetic anhydride is able to oxidise cyclohexene, α-pinene, tetralin, and other unsaturated compounds with formation of unsaturated ketones. It was later established[359] that this entails allylic oxidation:

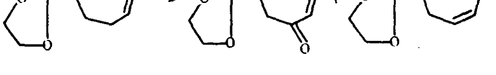


It was subsequently demonstrated that a more convenient reagent for allylic oxidation is di(t-butyl) chromate:[77]



Cholesteryl acetate also gives rise to quantitative yields of the ketone;[77] the reaction was carried out in a non-polar solvent with added acetic anhydride. The latter reagent has been used successfully for the oxidation of various terpenoids in the allyl position.[360–373] Cyclohexadiene and cyclopropene also react with hexavalent chromium at the allyl carbon–hydrogen bond.[374]

The reaction of dienes with PCC is of interest:[375]



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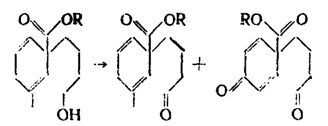
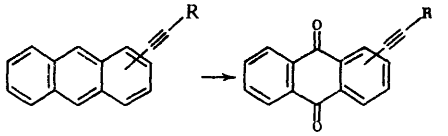
† Word(s) missing in Russian text. (Editor of Translation).

The 1,4-diene ester shown below is oxidised analogously in the allyl position:[376]

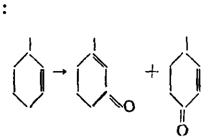


The oxidation of polynuclear aromatic hydrocarbons to quinones by chromium trioxide in acetic acid merits attention.[377] Alkylethynyl-substituted aromatic hydrocarbons are converted into quinones under similar conditions:[378]

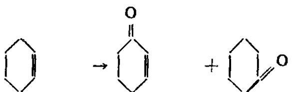


It is noteworthy that, in contrast to the manganese compounds which react rapidly with alkenes and alkynes[379,380] to form 1,2-diols and 1,2-diketones, chromium compounds (chromyl acetate,[358] chromic acid,[359] t-butyl chromate,[69] and the pyridine complex of chromium trioxide[381]), which are readily available and cheap oxidants,[382–385] interact slowly to form α-oxidation products.

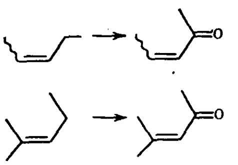
When substituted cyclohexenes and steroids interact with the dipyridine complex of chromium trioxide in methylene chloride, the allyllic methylene groups are oxidised slowly.[381] If there is more than one methylene group in the conformationally flexible molecule, then enones are obtained as a result of attack directed to a series of possible positions, while in a conformationally rigid system a rigorous selectivity of the oxidation reaction is observed; attack at the methine position (wherever this is possible) leads to the formation of the isomeric enone:



An analogous picture has been observed also in a sterically shielded methylene system, for example:[381]



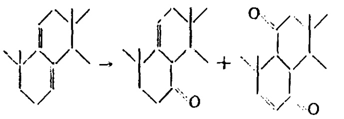
These reactions are characteristic also of substituted cyclopentenones.[386] The hexavalent chromium ion has been used also for the allylic oxidation of acyclic alkenes:[205]



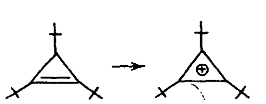
The allylic oxidation of alkynes has been demonstrated in two investigations.[254,387] Various internal alkynes react with chromium(VI) compounds to form α-diketones and allylic oxidation products, high yields of the latter being attained in the presence of the bipyridyl complex of chromium trioxide.[387]

When α-steryl acetate is made to react with chromic acid in acetic acid, allylic oxidation takes place together with epoxidation.[200] α-Cholestenyl acetate,[388] α-spinosterol,[202,203] and other polycyclic alkenes[204,205] react analogously.

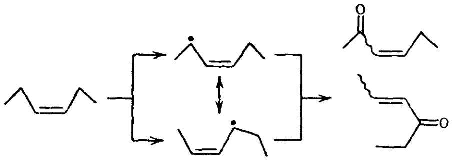
The reaction of steroid dienes, where allylic oxidation takes place with formation of diketones, is of special interest.[206–209]



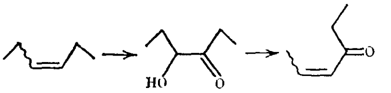
On the other hand, it has been estaalished that in the oxidation of a multiple bond in steroids the formation of ketols is also observed.[210–212] Cyclohexadiene reacts at room temperature with chromium trioxide in acetic acid with formation of benzene.[365] Under analogous conditions, tri(t-butyl)cyclopropene affords the tri(t-butyl)cyclopropenylium cation:[389]



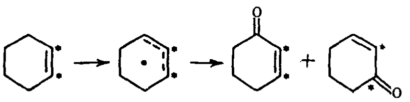
It has been suggested that allylic oxidation does not involve the initial attack on the multiple bond and proceeds either via the allyl radical or via a carbonium ion, which may lead to the isomerisation of the double bond, as is in fact observed in reality:[199]



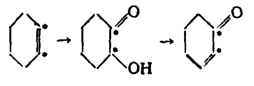
The initial oxidation of the multiple bond via epoxides to the corresponding hydroxyketones, which subsequently afford αβ-unsaturated ketones after eliminating water, has been suggested as an alternative:[210]



Since isomeric products are formed on oxidation, it has been postulated that the process proceeds via the first of the mechanisms postulated. Indeed, it has been established by the tracer atom method (at the multiple bonds) that both the methylene and methylidyne groups are oxidised in the reaction of cyclohexene with chromic acid:[199]



If the reaction proceeded via a hydroxyketone, then only one isomer would have been formed:



It is believed that an intermediate in which chromium is in the +4 oxidation state is obtained in allylic oxidation.[337,364]

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The data presented in this review demonstrate the extensive synthetic possibilities of the application of hexavalent chromium compounds as reagents in the chemistry of unsaturated compounds. Many oxidants, which are quite usual in organic chemistry, are unsuitable for alkenes, alkynes, alkadienes, enynes, etc. with functional groups as substituents. As regards chromium reagents, the most promising proved to be the coordination complexes of hexavalent chromium, in particular, the pyridine complexes. Pyridinium chlorochromate, which is irreplaceable in the generation of functional groups in highly unsaturated carbinols and polyols, is comparatively universal. However, one should note the impossibility of using it in the synthesis of compounds which are exceptionally sensitive to increased acidity and which can readily undergo prototropic transformations. The growing interest in chromium(VI) coordination complexes has led to the discovery of reagents with a less pronounced acidity: pyridinium dichromate, 2,2′-bipyridyl chlorochromate, and 4-(dimethylamino)pyridinium chlorochromate, as well as reagents on carriers and polymeric supports. For example, the possibility of the selective oxidation of diene carbinols by 4-dimethylaminopyridinium chlorochromate has been demonstrated. Chromyl nitrate proved to be irreplaceable in the stereospecific epoxidation of dienes. An interesting approach to the formation of acetylenic epoxides involving the chemoselective oxidation of enynes by chromyl chloride has been discovered.

The main bulk of studies on the oxidation of unsaturated systems having functional groups as substituents by chromium reagents are not only of theoretical but also of practical importance and can find further applications in the construction of natural structures and in the synthesis of hormones, pheromones, prostaglandins, and their synthones. In the future, the studies in this field will in all probability be directed to finding new oxidising systems, which will permit smooth regiospecific, chemospecific, and stereospecific syntheses.

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The Interaction of Carbenes and Nitrenes with Azo-compounds

A.A.Suvorov and M.A.Kuznetsov

A critical analysis of the literature on the interaction of carbenes and nitrenes with azo-compounds is presented, attention being concentrated on the reactions of aminonitrenes.
The bibliography includes 83 references.

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I. INTRODUCTION

The study of the reactions of unstable intermediate species is one of the most fruitful "growth points" in modern organic chemistry. Its branches, such as the chemistry of carbonium ions, carbanions, and free radicals, have already become classical but at the same time it continues to develop vigorously. During the last decades, very much attention has been devoted to the study of the reactions of carbenes, nitrenes, and their analogues—neutral intermediates incorporating an atom with an incomplete six-electron (sextet) electron shell. Owing to the exceptional wide variety of reactions of such compounds, which has stimulated both applied, synthetic development and numerous studies by theoreticians (see, for example, the corresponding chapters in the annual reviews "Organic Reaction Mechanisms" or "Annual Reports on the Progress in Chemistry").

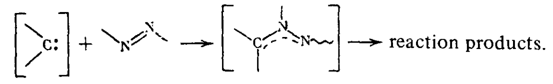
The most important trend in this field concerns the study of the interaction of carbenes and nitrenes with unsaturated groups. Their addition to the C=C, C≡C, and C=X (X is a heteroatom) bonds constitutes an effective general method of synthesis of three-membered rings, strained polycyclic systems, and a very great variety of products of further reactions. This is why thousands of papers and tens of reviews and monographs have been devoted to the above branch of chemistry of carbenes and their analogues and their number continues to grow.

Azo-compounds have been one of the few exceptions in this field and the interaction of carbenes and nitrenes with compounds containing the N=N group has not been investigated systematically until recently. However, since the beginning of the 1970s, a whole series of studies have been carried out in which it has been demonstrated that the usually fairly inert azo-group reacts smoothly with these sextet species to form new classes of unusual polynitrogen compounds. So far, fairly extensive data have accumulated in this field requiring a survey, which has been the reason why this review, in which we have tried to cover the literature until the beginning of 1985, has been written.

II. THE ADDITION OF CARBENES TO AZO-COMPOUNDS

In contrast to the majority of other reactions, the reaction with azo-compounds has been investigated in less detail for carbenes than for nitrenes. Furthermore, it has been found that certain reactions, assigned to this type, in reality proceed without the participation of carbenes. Thus investigation of the kinetics of the reactions of diazo-compounds with a series of azo-compounds, in the first place with azodicarbonyl compounds, showed that the initial diazo-compound itself usually reacts with the azo-group and that only then is the nitrogen molecule split off[1] (among the later studies in this field see, for example, Korobitsyna and co-workers[2,3] and the literature quoted therein).

Nevertheless, it has been suggested that in many instances it is precisely carbenes that react with azo-compounds. This entails the formation, as a rule, of the corresponding 1:1 adducts to which the structure of diaziridines or the isomeric 1,3-dipolar compounds—azomethineimines (I)—was attributed in early studies. Later it was demonstrated that in reality the reaction products have a different structure and can be usually formally regarded as a result of the 1,4-addition of the carbene to the N=N−C=X fragment (X = O, N, or C) of the initial conjugated azo-compound. However, although the azomethineimines (I) are not in fact the final products in any of the reactions of carbenes with azo-compounds known at the present time, their involvement as intermediates has been suggested:



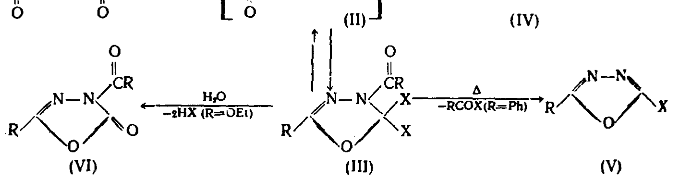
(I)

The reactions of carbenes with azo-compounds can be divided into several types: interaction of dihalogeneocarbenes with azo-compounds; the addition of methylene and its aromatic derivatives to 2,2'-azopyridine and its analogues; the addition of alkylidenecarbenes to aromatic azo-compounds and the reaction of alkoxyalkylcarbenes with oxadiazolines.

1. The Reactions of Dihalogenocarbenes with Azo-Compounds

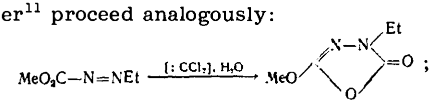
In reactions with various azo-compounds dihalogeneocarbenes were usually generated by the thermal decomposition of trihalogenomethylphenylmercury[4-8] or sodium trichloroacetate.[4,5,9] The addition of dihalogeneocarbenes to azodicarbonyl compounds has been studied in greatest detail:

$$\mathrm{PhHgCX_2Br} \xrightarrow[-\mathrm{PhHgBr}]{20\,^\circ\mathrm{C\ or\ }\Delta} [:\mathrm{CX_2}] \xleftarrow[-\mathrm{NaX},\,-\mathrm{CO_2}]{\Delta} \mathrm{CX_3CO_2Na}\ ;$$
$$\mathrm{X_2{=}Cl_2,\ ClBr,\ Br_2}$$



At room temperature, the products in this instance are oxadiazolines (III), which are apparently formed as a result of the cyclisation of the intermediate azomethineimines (II).[4-8] If the reaction is carried out with heating, then, depending on the nature of the substituent, the oxadiazolines (III) are either rearranged to the hydrazones (IV), probably again via the azomethineimines (II),[4,5] or they split off the RCOX molecule with formation of the oxadiazoles (V);[6,7] in the presence of water, the main reaction products are the oxadiazolinones (VI).[9]

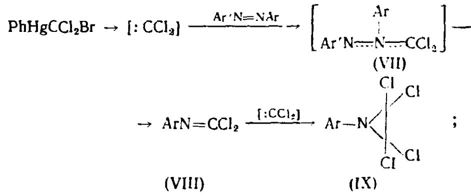
The addition of dichlorocarbene to methyl ethylazocarboxylate (in the presence of water)[9] and to bis(trimethylsilyl)diimide[10] and also the addition of dicyanocarbene, generated by the decomposition of dicyanodiazomethane, to azodicarboxylic ester[11] proceed analogously:



$$\mathrm{Me_3SiN{=}NSiM_3 \xrightarrow{[:\,CCl_2]} (Me_3Si)_2N{-}N{=}CCl_2}\ ;$$

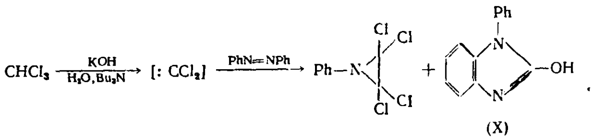
$$\mathrm{EtO_2CN{=}NCO_2Et \xrightarrow{[:\,C(CN)_2]} (EtO_2C)_2N{-}N{=}C(CN)_2}\ .$$

Dichlorocarbene reacts significantly differently with azoarenes. In this case, the phosgeneimines (VIII) and the products of the further addition of the carbene (IX) are formed in this reaction:[4,8]



Ar = Ph, *p*-Tol, *p*-ClC$_6$H$_4$.

When dichlorocarbene was generated by the phase transfer method, the formation of phosgeneimine in the reaction with azobenzene was not noted, but 2-hydroxy-1-phenylbenzimidazole (I) was islated as an additional product:[12]

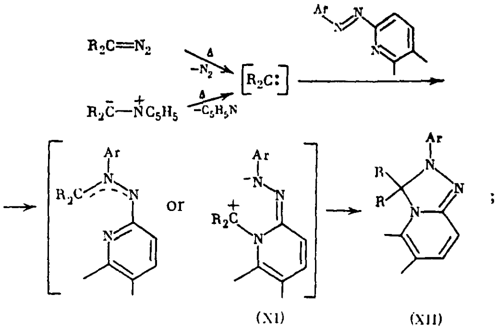


It has been suggested that the azomethineimines (VII) [8] (or the isomeric diaziridines[8,12]) are formed initially in this instance and then lose an arylnitrene[8] or rearrange to benzimidazole derivatives (cf. the Section below). The mechanism of the elimination of the arylnitrene was not discussed.[8] It may be that the intermediate azomethineimines (VII) react with a second molecule of dichlorocarbene to form two phosgeneimine molecules.

The same products are obtained also in the reaction of dichlorocarbene with azoxyarenes, probably as a result of the intermediate formation of azo-compounds.[8,12]

2. The Addition of Methylene and Arylcarbenes to 2,2′-Azopyridine and Its Analogues

The reactions of methylene and its aryl-substituted derivatives with 2,2′-azopyridine, 2-phenylazopyridine, and 2,2′-azoquinoline involve the formation, like the reactions of dihalogeneocarbenes with azodicarbonyl compounds, of (formally) the products of the 1,4-addition of the carbene to the N=C—N=N fragment, namely the triazolopyridines (XII).[13,14] The carbenes were generated by the thermolysis of the corresponding diazo-compounds or pyridinium ylides:

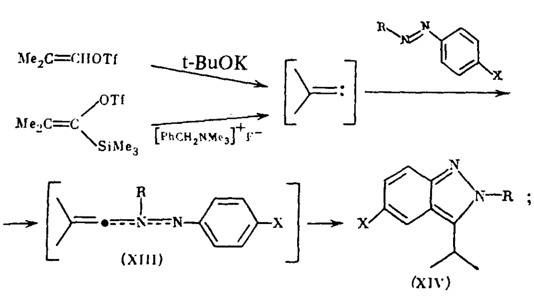


R = H, Ph: R$_2$C = PhCH, 9-fluorenylidene;
Ar = Ph, 2-pyridyl, 2-quinolinyl.

The authors of the first studies of this reaction[15,16] assumed that carbenes are not formed in the course of the reaction. However, it was shown later[13] that the interaction of diazo-compounds with 2,2′-azopyridine and its analogues proceeds only under these conditions when the diazo-compounds are unstable and decompose with formation of carbenes. The rate of reaction then varies with temperature, like the rate of decomposition of the initial diazo-compound in the absence of substrates, which indicates the carbene mechanism of this reaction.[13] However, it is noteworthy that, apart from the azo-group, the molecules of 2,2′-azopyridine and its analogues contain yet another potential reaction centre—the nitrogen atom of the pyridine ring and it is not known whether the initial attack is in fact directed to the azo-group or whether an alternative mechanism with formation of the intermediates (XI) operates.[13]

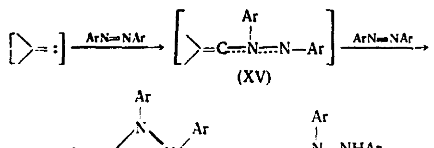
3. The Addition of Alkylidenecarbenes to Azoarenes

The reaction of 2-propylidenecarbene with a number of azoarenes and t-butylazobenzene results in the formation of, formally, the products of the 1,4-addition of the carbene to the N=N—C=C system, probably via the intermediate azomethineimines (XIII):[17-20]



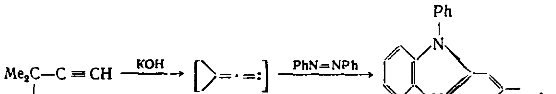
OTf = OSO$_2$CF$_3$; R = T-Bu, *n* = YC$_6$H$_4$; X, Y = H, Me, OMe, F, Cl .

The reactions with asymmetric substrates yield comparable amounts of both possible isomeric benzopyrazoles (XIV).[18,19] In the reactions with azoarenes containing strong electron-accepting substituents, the 2 : 1 adducts (XVI) or (XVII), regarded as the results of the 1,3-dipolar addition of the intermediate azomethineimines (XV) to the initial azo-compound, were isolated in low yields:[19,20]



Ar=4-$CF_3C_6H_4$, 3,5-$(CF_3)_2C_6H_3$.

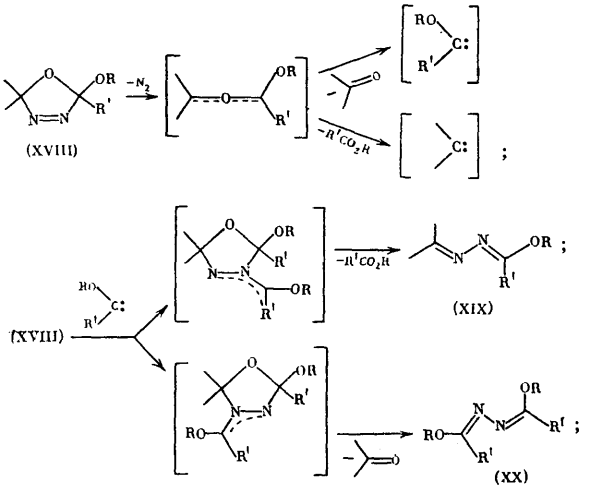
The initial adducts of dimethylvinylidenecarbene with azobenzene rearrange with dissociation of the nitrogen–nitrogen bond:[21]



The reaction of fluorenylidenecarbene with azobenzene leads to the formation of a small amount of a 1 : 1 adduct, whose structure has not, however, been established.[22]

4. The Reaction of Alkoxycarbenes with 1,3,4-Oxadiazol-3-ines

The thermal decomposition of a series of 2-alkoxy-1,3,4-oxadiazol-3-ines (XVIII) results in the formation of dialkyl- and alkylalkoxy-carbenes, which react with the initial compounds:[23]



R = Me, Et, CH_2CF_3, CH_2CCl_3; R' = Me, Et, iso-Pr; RR' = $(CH_2)_3$.

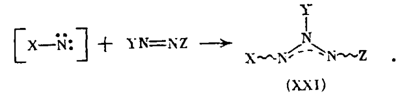
The main reaction pathway involves the intermediate formation of alkoxycarbenes and the subsequent addition to the nitrogen atom in the 3-position in the oxadiazoline ring, which ultimately leads to the asymmetric azines (XIX).[23] However, the reaction mixtures usually contain also the azine (XX) and dimethylketazine, which the authors[23] regard as a result of the participation in the reaction of not only the alkoxycarbene but also of dimethylcarbene.

III. THE ADDITION OF NITRENES TO AZO-COMPOUNDS

A fairly large range of examples of the interaction of nitrenes with azo-compounds has now been investigated. It has been found that the addition takes place only in those cases where the substituents in the nitrene and in the azo-compound differ greatly in their electronic nature. On the other hand reactions with participation of many nitrenes such as aryl-, perfluoroalkyl-, amino-, and imido-nitrenes as well as others frequently result in the formation of their formal dimers—azo-compounds[24]—in high yields, but there have been no communications about the products of further addition of nitrenes to these compounds. This indicates most probably the inertness or low reactivity of nitrenes in relation to azo-compounds having the same substituents (although one cannot rule out also the possibility that nitrenes do nevertheless add in this instance by the resulting adducts are unstable and decompose with formation of the initial azo-compound).

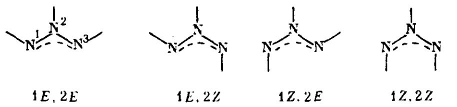
In our view, this type of dependence of the reactivity of nitrenes in relation to azo-compounds on the electronic nature of the substituents justifies the assumption that, when the nitrene molecule contains electron-donating substituents and the azo-compound molecule contains electron-accepting substituents (as in the reactions of dialkylamino- and diarylamino-nitrenes with azodicarboxylic acid derivatives), the addition of the nitrene to the azo-group is nucleophilic, while in the opposite case (the addition of phthalimidonitrene and alkoxycarbonylnitrenes to azoalkanes and azoarenes) this interaction is electrophilic.

In contrast to the addition of carbenes, where the formation of azomethineimines as intermediates is usually postulated, almost all the known reactions of nitrenes with azo-compounds lead to stable 1,3-dipolar compounds—the azimines (XXI):



(XXI)

E,*Z*-isomerism is possible in relation to both partially double nitrogen–nitrogen bonds and the azimines containing different substituents at the terminal nitrogen atoms can exist in principle in the form of four stereoisomers:

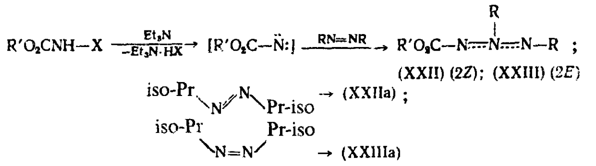


A non-empirical calculation of the relative stabilities of the isomers of the simplest azimine N_3H_3 [25] showed that the *Z*,*Z*-isomer is the most stable, that the energy of the *E*,*Z*-configuration is slightly higher, and that the *E*,*E*-structure is energetically extremely unfavourable. Taking into account steric factors, one may expect that the *E*,*Z*- and *Z*,*E*-isomers will be the most stable for the substituted azimines and that in all the known acyclic azimines the two nitrogen–nitrogen bonds do indeed have the opposite configurations.

1. The Addition of *C*-Nitrenes to the Azo-Group

As mentioned above, arylnitrenes and a series of other *C*-nitrenes apparently do not react with azo-compounds containing the same substituents as those in the nitrene molecule. In particular, the reaction of azocycarbonylnitrene with diethyl azodicarboxylate could not be achieved.[26,27]

On the other hand, alkoxycarbonylnitrenes add to nitrogen-containing compounds without electron-accepting substituents—azoalkanes and azoarenes—with formation of the esters of the corresponding azimine-1-carboxylic acids (XXII) or (XXIII):[28,29]


(XXII) (2*Z*); (XXIII) (2*E*)

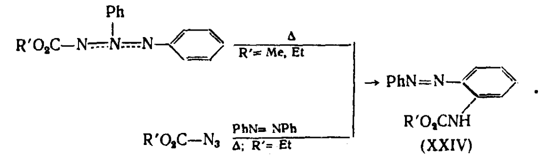
(XXIIa); (XXIIIa)

$X = OSO_2C_6H_4NO_2$-*p*; R′ = Me, Et; R = iso-Pr (a), Ph (b), *p*-Tol (c); R_2 = 1,3-cyclopentylene (d).

The alkoxycarbonylnitrenes were generated under mild conditions by the α-elimination of *p*-nitrobenzenesulphonic acid from the corresponding sulphonyloxycarbamates in the presnece of an equimolar amount or an excess of the azo-compound.

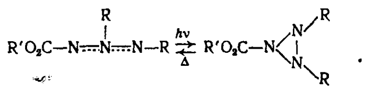
The reaction with *E*- and *Z*-2,2′-azopropanes proceed with retention of the configuration of the azo-group and lead respectively to 2*Z*- and 2*E*-azimines (XXIIa) and (XXIIIa).[28,29] On the other hand, the same product, whose geometry has not been established, is formed from the isomeric *E*- and *Z*-azoarenes.[29]

The adducts of alkoxycarbonylnitrenes with azobenzene rearrange on heating with migration of the alkoxycarbonylimino-group to the *ortho*-position in the benzene ring and the formation of the products (XXIV).[29] The same substances are formed on thermolysis of ethoxycarbonyl azide in the presence of azobenzene:[30,31]

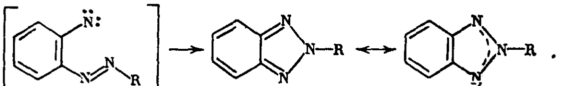

(XXIV)

Probably ethoxycarbonylnitrene adds in this instance to azobenzene with subsequent thermal rearrangement of the adduct (XXIIb) or (XXIIIb).[30,31]

It is of interest to note that derivatives of a three-membered ring with three nitrogen atoms, namely triaziridines (XXV), were obtained for the first time by the cyclisation of the azimines (XXIIa) and (XXIIId).[28,32] These compounds are comparatively unstable and gradually recyclise to the initial azimines even at room temperature:[28,32]

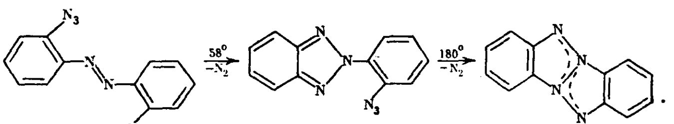

(XXIIa), (XXIIIg)

In contrast to carbonylnitrenes, alkyl- and aryl-nitrenes have been much more rarely introduced into intermolecular reactions[24] and there are no examples in the literature of their interaction with azo-compounds. However, a series of reactions which can be formally treated as intermolecular addition of arylnitrenes to the azo-group, usually located in the *ortho*-position, have already been known for more than 100 years:


(XXVI)

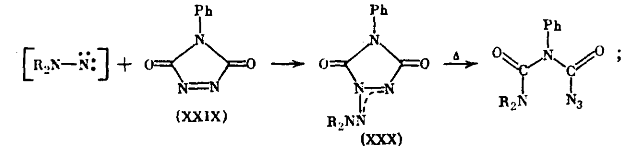
The oxidation of *o*-aminoazo-compounds by various oxidants,[33-39] the reduction of *o*-nitroazo-compounds,[40-44] and the thermolysis and photolysis of the corresponding azides[31,34,45-50] belong to these reactions. Their products are 2*H*-benzotriazoles (XXVI), related to azimines, or the initial heterocyclic compounds containing the azimine chain in their structure.

However, in the majority of cases the reactions enumerated above apparently proceed via intermediate species other than nitrenes[38] and also as concerted processes.[45] The involvement of nitrenes is assumed in this instance by analogy with other reactions,[41-43] is regarded as one of the possible variants, and as a rule has not been reliably demonstrated (cf. for example, Butler[38] and Dyall,[39] Spagnolo et al.,[47] Spagnolo et al.,[48] etc.); at the same time even formally very similar compounds can have different mechanisms. As an illustration, one may quote a series of syntheses of tetraazapentalene systems of type (XXVIII),[51-55] where it has been demonstrated, in relation to the thermolysis of *oo*′-diazidoazobenzene (XXVII), that the elimination of the first nitrogen molecule is a concerted process and that the nitrene mechanism is possible only for the second stage (but has not been demonstrated):


(XXVII) (XXVIII)

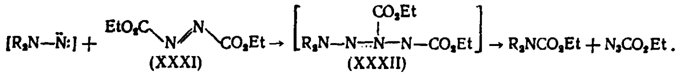
2. The Interaction of Dialkylamino- and Diarylamino-nitrenes with Derivatives of Azodicarboxylic Acid

The first communication about the reaction of aminonitrenes and nitrenes in general with nitrogen-containing compounds was published in 1970.[56] In this and in a series of later studies it was shown that dialkylamino- and diarylaminonitrenes add to 4-phenyl-1,2,4-triazoline-3,5-dione (XXIX), a cyclic derivative of azodicarboxylic acid, with formation of the stable adducts (XXX),[56,57] the azimine structure of which has been confirmed by ^{1}H NMR, IR, and UV spectra, as well as mass spectra and, in the case of the adduct of diphenylaminonitrene (XXXa), also by X-ray diffraction.[58] On heating, the aminoazimines (XXX) rearrange with the opening of the five-membered ring:[56,59]


(XXIX) (XXX)

R = Ph (a), CH_2Ph (b), Me (c), Et (d); R_2N– = MePhN– (e), $(CH_2)_5N$–(f).

The reaction of the same aminonitrenes with diethyl azodicarboxylate (XXXI) leads in each instance to a mixture of the corresponding urethane with ethoxycarbonyl azide, but the full analogy of this set of substances with the products of the thermolysis of the azimines (XXX) makes it possible to postulate also the intermediate formation of the aminoazimines (XXXII):[56,60,61]


(XXXI) (XXXII)

The high thermal stability of the cyclic aminoazimines (XXX) has been explained by the fact that the migration of the carbonyl group to the amino-nitrogen atom is hindered in this instance by steric factors.[60]

The aminonitrenes were generated in these reactions by oxidising the corresponding 1,1-disubstituted hydrazines using azodicarbonyl compounds as oxidants;[56,60,61] in addition, dibenzylaminonitrene was obtained by decomposing dibenzylamino-*N*-azide:[57]

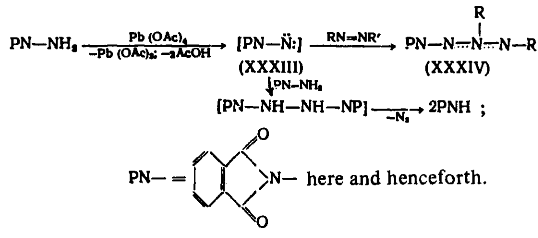
$$R_2N{-}NH_2 \xrightarrow[-XNHNHX]{XN{=}NX} [R_2N{-}\ddot{N}{:}] \xleftarrow[R=CH_2Ph]{-N_2} R_2N{-}N_3 \, .$$

The involvement of aminonitrenes in the reaction is indicated by the following data. Firstly, the same aminoazimine (XXXb) is formed from both 1,1-dibenzylhydrazine and from dibenzylaminoazide in the reaction with triazolinedione (XXIX) and in the latter case the rate of decomposition of the azide (the rate of evolution of nitrogen) is independent of the presence of the azo-compound (XXIX) in the mixture.[56] Secondly, in the reaction of 1,1-disubstituted hydrazines with azodicarboxylic ester (XXXI) the formation of a small amount of tetrazenes—typical products of the interaction of aminonitrenes with the initial hydrazines—was observed and the yield of the tetrazenes increased greatly (sometimes by a factor of hundreds) when the azo-compound was added to hydrazine instead of *vice versa*.[56,60,61]

3. The Interaction of Phthalimidonitrene with Azo-Compounds

Among all the sextet species, phthalimidonitrene (XXXIII) has been studied in greatest detail in its reaction with azo-compounds. Its addition to the azo-group was first reported in 1971 [62] and since then many studies have been devoted to this reaction and its products.[62–81]

In all cases, phthalimidonitrene (XXXIII) was generated by oxidising *N*-aminophthalimide with lead tetraacetate in the presence of an equimolar amount of an azo-compound:

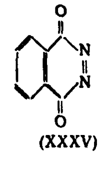


$$PN{-}NH_2 \xrightarrow[-Pb(OAc)_2;\,-2AcOH]{Pb(OAc)_4} \underset{(XXXIII)}{[PN{-}\ddot{N}{:}]} \xrightarrow{RN=NR'} \underset{(XXXIV)}{PN{-}N{=}\overset{R}{\overset{|}{N}}{=}N{-}R'} \, ;$$

$$\downarrow^{PN-NH_2}$$

$$[PN{-}NH{-}NH{-}NP] \xrightarrow[-N_2]{} 2PNH \, ;$$

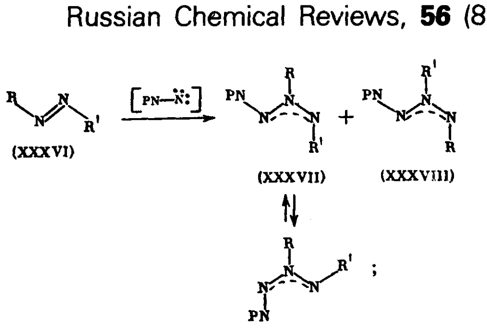
Phthalimidonitrene (XXXIII) adds readily and with high yields (up to 95%) to substrates containing hydrocarbon substituents at the azo-group with formation of 2,3-disubstituted 1-phthalimidoazimines (XXXIV), but it does not react with the azodicarbonyl compounds (XXXI) and (XXXV).[30,31]



(XXXV)

Phthalamide, formed apparently as a result of the interaction of the nitrene (XXXIII) with the initial *N*-aminophthalimide, is usually a side product of the reaction.[82] The structure of the reaction products has been established by spectroscopic methods (^{1}H and ^{13}C NMR, UV, etc.) and also by X-ray diffraction for 1*E*, 2*Z*- and 1*Z*, 2*E*-2,3-dimethyl-1-phthalimidoazimines (XXXVIIa) and (XXXIXa).[64,65]

The addition of phthalimidonitrene (XXXIII) to *E*-azoalkanes (XXXVI) proceeds stereospecifically with retention of the configuration of the azo-group and fully stereoselectively,[67,68] leading to 1*E*, 2*Z*-2,3-dialkyl-1-phthalimidoazimines (XXXVIIa) and (XXVIIIa):[62,63,66–68]



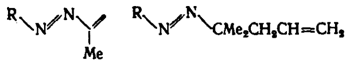
(XXXVI) (XXXVII) (XXXVIII)

(XXXIX)

R = R' = Me (a), Et (b), iso-Pr (c), CHMePh (d);
R = Me, R' = Et (e), iso-Pr (f), t-Bu (g), CH$_2$CH$_2$CH = CH$_2$ (h);
R' = iso-Pr, R = Et (i), CH$_2$CH$_2$CH = CH$_2$ (j), CHMeCH$_2$CH = CH$_2$ (k).

The asymmetric *E*-azoalkanes (XXXVI, e–g and I) give rise to mixtures of the regioisomeric 2,3-dialkyl-1-phthalimidoazimines (XXXVII) and (XXXVIII) with predominance of the isomer (XXXVII) containing a smaller substituent at the central nitrogen atom of the azimine system.[67,68] The regioselectivity of the reaction increases on passing from *E*-methylazoethane (XXXVIe) to the more asymmetric substrates (XXXVI, f and g).[67,68]

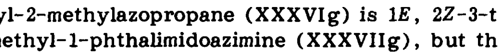
The reaction of phthalimidonitrene with γδ-unsaturated analogues of *E*-azoalkanes (XXXVI, h, j, and k) proceeds fully analogously.[69] The addition of the nitrene to the azo-group only is then observed; the products of addition to the C=C bond were not detected.[69] However, αβ-unsaturated azo-compounds—*E*-2-alkylazopropenes (XL)—proved to be extremely inert in relation to phthalimidonitrene.[69] The reasons for this are obscure.



(XL) (XLI)
R = Me, iso-Pr.

When a tertiary substituent is introduced at the azo-group, the reactivity of *E*-azoalkanes diminishes sharply.[67–69] The addition of phthalimidonitrene to *E*-2-methyl-2-methylazopropane (XXXVIg) can be achieved only by employing a special method whereupon the side reaction involving the formation of phthalimide is suppressed [even in this case most of the azo-compound (XXXVIg) is preserved in the course of the reaction[67,68]] and the reaction with unsaturated tertiary azo-compounds (XLI) could not be carried out at all.[69] The main product of the addition of phthalimidonitrene to *E*-2-methyl-2-methylazopropane (XXXVIg) is 1*E*, 2*Z*-3-t-butyl-2-methyl-1-phthalimidoazimine (XXXVIIg), but the reaction is overall more complex than that with the sterically unhindered *E*-azoalkanes (XXXVI, a–f and i) and small amounts of unstable products, whose structure has not been established, are formed.[67,68]

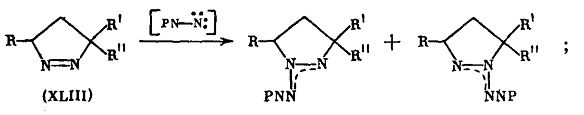
The reaction of phthalimidonitrene with *Z*-2,2'-azopropane (XLII) affords a high yield of 1*Z*, 2*E*-2,3-diisopropyl-1-phthalimidoazimine (XXXIXc), which, however, is configurationally extremely unstable and is readily converted into the 1*E*, 2*Z*-isomer (XXXVIIc):[66]



$$\text{iso-Pr}{-}N{=}N{-}\text{Pr-iso} \xrightarrow{[PN-\ddot{N}:]} (XXXIXc) \rightarrow (XXXVIIc).$$

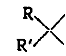
(XLII)

The addition of phthalimidonitrene to cyclic analogues of azoalkanes with a fixed *Z*-configuration of the azo-group, namely 1-pyrazolines (XLIII, a–d)[67,69,70] and 2,3-diazabicyclo]2.2.1]hept-2-ene (XLIIIe),[66] leads to the corresponding 2,3-trimethylene-1-phthalimidoazimines (XLIV) and (XLV). The reaction with asymmetric 1-pyrazolines (XLIII, b–d) leads to the formation of two regioisomeric adducts (XLIV) and (XLV), in each case with the sterically less hindered isomer (XLIV) predominating,[67,69,70] i.e. the influence of the bulk of the substituents on the mode of reaction is in this case qualitatively the same as in the series of acyclic *E*-azo-compounds. At the same time, the yields of the adducts with the cyclic azo-compounds (XLIII) are higher than for the adducts with the *E*-azoalkanes (XXXVI);[66,67,70] even for the adducts with 1-pyrazolines (XLIII, c and d), formally containing a tertiary substituent at the azo-group, the reaction proceeds without complications and leads to both regioisomeric adducts (XLIV, c and d) and (XLV, c and d).[67,70] This can apparently be accounted for by the greater steric accessibility of the azo-group when it has the *Z*-configuration



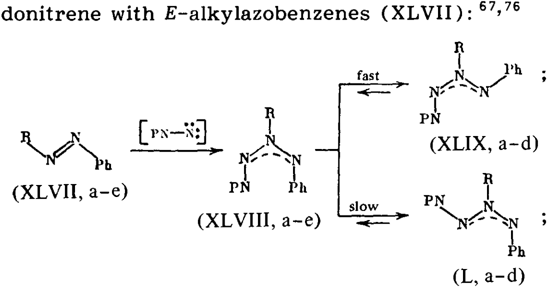
R = R′ = H, R″ = H (a), Me (b); R′ = R″ = Me, R = H (c), Me (d); RR′ = 1,3-cyclopentylene, R″ = H (e).

On the other hand, 3*H*-diazirines (XLVI), both mono- and di-substituted, proved be be almost inert in relation to phthalimidonitrene,[67,69] which is evidently associated with the relatively deep position of the highest occupied molecular orbital in these compounds:[83]


R = H, R′ = t-Bu, Ph; R = Me, R′ = Et; RR′ = $(CH_2)_5$

(XLVI)

The reaction of phthalimidonitrene with the markedly asymmetric *E*-alkylazobenzenes (XLVII)[67,71–76] takes place stereospecifically with retention of the configuration of the azo-group and usually fully regioselectively and stereoselectivity with formation of 1*Z*, 2*Z*-2-alkyl-3-phenyl-1-phthalimidoazimines (XLVIII).[67,74,76] With the exception of the t-butyl derivative (XLVIIIe), the latter are unstable at temperatures above approximately 0 °C and rapidly equilibrate in solution with 1*Z*, 2*E*-azimines (XLIX) and much more slowly with the 1*E*, 2*Z*-isomers (L). The principal components of the equilibrium mixtures of stereoisomers are 1*Z*, 2*E*-azimines (XLIX).[67,75,76] Their rapid formation from the intermediate 1*Z*, 2*Z*-isomers (XLVIII) leads to the apparent inversion of the configuration of the azo-group in the reaction of phthalimidonitrene with *E*-alkylazobenzenes (XLVII):[67,76]

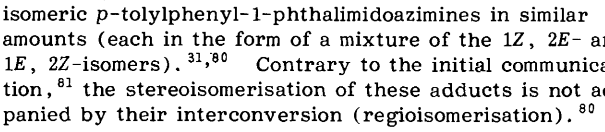


R = Me (a), Et (b), Pr (c), iso-Pr (d), t-Bu (e).

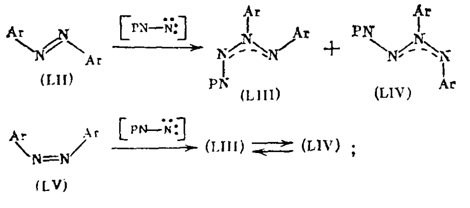
With increase of the bulk of the alkyl substituent, the relative stability of the 1*Z*, 2*Z*-isomers (XLVIII) and hence their equilibrium content increase sharply.[67,75] As a result, 1*Z*, 2*Z*-2-t-butyl-3-phenyl-1-phthalimidoazimine (XLVIIIe) is configurationally completely stable and is the first example of a stable acyclic 1*Z*, 2*Z*-azimine.[67,74,75]

The kinetically controlled formation of 1*Z*, 2*Z*-azimines (XLVIII) in the reaction of phthalimidonitrene with *E*-alkylazobenzenes (XLVII) can probably be accounted for by secondary orbital interactions stabilising the *cis*-disposition of the phthalimide group of the nitrene and of the phenyl substituent of the azo-compound in the transition state.[67,76] One cannot rule out that the same interactions determine also the regioselectivity of the reaction.

The possible breakdown of regioselectivity in the addition process has been noted only for *E*-isopropylazobenzene (XLVIId). In this case, the regioisomeric 1*E*, 2*Z*-3-isopropyl-2-phenyl-1-phthalimidoazimine (LI) (25% of the overall amount of adducts) is apparently formed together with the adducts (XLVIIId), (XLIXd), and (Ld):[67,75]



The reaction of phthalimidonitrene with *E*-azoarenes (LII) yielded mixtures of 1*Z*, 2*E*- and 1*E*, 2*Z*-2,3-diaryl-1-phthalimidoazimines (LIII) and (LIV),[31,62,63,77–81] between which equilibrium is gradually established at room temperature. Here the main reaction products are 1*Z*, 2*E*-azimines (LIII) and their content in the mixtures of isomers isolated exceeds somewhat the equilibrium value:[63,80]



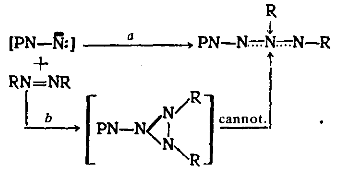
Ar = Ph (a), *p*-Tol (b).

The mechanism of the addition has not been investigated in detail, but, by analogy with *E*-alkylazobenzenes (XLVII), presumably the preferential inversion of the configuration of the azo-group can be explained in this case too by the rapid stereoisomerisation of the intermediate 1*Z*, 2*Z*-2,3-diaryl-1-phthalimidoazimines.[67,76]

The addition of phthalimidonitrene to *Z*-azoarenes (LV) leads to 1*Z*, 2*E*-2,3-diaryl-1-phthalimidoazimines (LIII) with a small admixture of the 1*E*, 2*Z*-isomers (LIV)[62,63,77–80] probably owing to the partial stereoisomerisation of the primary products (LIII). As for other types of azo-compounds, the yields of 1-phthalimidoazimines in the reaction with *Z*-azoarenes are much higher than in the reaction with the *E*-isomers.[62,63,77–80]

The reactions of phthalimidonitrene with both *E*- and *Z*-4-phenylazotoluenes result in the formation of both regioisomeric *p*-tolylphenyl-1-phthalimidoazimines in similar amounts (each in the form of a mixture of the 1*Z*, 2*E*- and 1*E*, 2*Z*-isomers).[31,80] Contrary to the initial communication,[81] the stereoisomerisation of these adducts is not accompanied by their interconversion (regioisomerisation).[80]

The most probable mechanism of the addition of phthalimidonitrene to azo-compounds, which can explain almost all the features of this reaction, involves electrophilic attack on the sextet nitrogen atom via the highest non-bonding orbital of the azo-group, in actual fact via the unshared electron pair of one of the nitrogen atoms. In this single-stage process, the azimine π-electron system is formed together with the N–N σ-bond; according to experimental data, the reaction should proceed with retention of configuration (pathway *a*):



The alternative two-stage mechanism with the intermediate formation of triaziridine (pathway *b*) is significantly less realistic.[67,68,76]

Within the framework of the single-stage mechanism, it is possible to explain satisfactorily the influence of electronic and steric factors on the course of the reaction of phthalimidonitrene with azo-compounds.[67,68,76] Furthermore, we we are justified to expect that the principal features of the reactant—substrate interaction will be retained also for the electrophilic addition of other sextet species via the azo-group, i.e. that this mechanism will prove valid for a wide range of related objects.

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The Molecular-crystal Structure of Cellulose

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The structural models of the principal polymorphic varieties of cellulose proposed by different workers during the last two decades are analysed, the results obtained by the main structural methods are considered, and the reliability of a particular structural model is estimated. The ambiguity of the solution of the structural problems for cellulose in the cases of the existing diffraction data, even when stereochemical and packing limitations are invoked, is demonstrated. The results of semiempirical energy calculations for the stable structure of cellulose are discussed.
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I. INTRODUCTION

The processes occurring in the industrial processing of cellulose are as a rule heterogeneous and take place under diffusional conditions, which determines the dependence of the degree and kinetics of the reactions occurring on the structure of the solid polymer phase.

Several hierarchical levels of structural organisation can be differentiated in cellulose. These are the supermolecular structure with a characteristic distance ranging from several tens of angstroms and above and two lowest levels—crystalline and molecular, with characteristic distance of one angstrom. The higher structural levels are readily susceptible to study by electron and optical microscopic methods and low angle X-ray diffraction and have been fairly fully investigated.[1–8] The study of the molecular-crystal structure of cellulose constitutes the main problem.

Cellulose was one of the first polymers subjected to structural analysis. However, despite the large number of crystallographic studies of cellulose, the detailed structure of the crystalline region still remains the subject of extensive controversy.[9–11] This applies to all the known polymorphic varieties of cellulose, including the most thoroughly investigated varieties—cellulose I (CI, native) and cellulose II (CII, regenerated and mercerised). A large number of structural models, which conflict as regards fundamental characteristics such as the symmetry of the crystal lattice, the relative orientation of the chains, and the system of hydrogen bonds let alone even finer structural details, have been proposed.

The present review analyses the literature data on the molecular and crystal structures of CI and CII, the principal results of the structural investigations are considered, and the reliability of the existing concepts and structural models is estimated.

II. GENERAL INFORMATION ABOUT THE STRUCTURE OF CELLULOSE

Cellulose (C) consists of poly-(1 → 4)-β-D-glucopyranose, $(C_6H_{10}O_5)_n(C_6H_{12}O_6)_2$, where n (the degree of polymerisation) varies in the range 800–8000 depending on the nature of the specimen.[9–13] The structural formula of cellulose is presented in Fig.1, which also indicates the numbering of the atoms adopted in the stereochemistry of sugars and carbohydrates.[14–21]

1. The Symmetry and Parameters of the Unit Cell

The principal source of information about the molecular-crystal structure of cellulose is X-ray diffraction of highly oriented fibres. Typical X-ray diffraction patterns of cellulose contain darkened regions distributed continuously along layer lines which are caused by the one-dimensional diffraction and characterise the degree of ordering of the centres of gravity of the scattering molecules. The discrete spots of different intensity are due to three-dimensional diffraction. The number of independent spots of this type does not usually exceed 30–40.

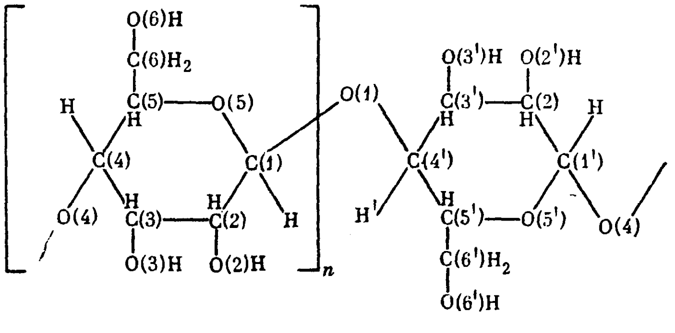

Figure 1. The structural formula of cellulose.

The paucity of the diffraction pattern is to some extent characteristic of the X-ray diffraction of polymers,[22–24] but, compared with the majority of synthetic polymers, the X-ray diffraction patterns of cellulose exhibit a steeper decrease of intensity with increase of the Bragg angle, which additionally limits the region of the possible reflections.[25] Such decrease of intensity can be caused either by the intense thermal movement of the structural elements of cellulose or by statistical disorder.

The only symmetry element of the crystal structure of cellulose is a twofold screw axis parallel to the axis of the fibre (space group $P2_1$).[25] The presence of this axis is indicated by the systematic extinction of the $00l$ reflection $l = 2n + 1$ on the X-ray diffraction patterns of cellulose.

Among the observed reflections, the strongest are the $hk0$ reflections, the most intense being those for which $h + k = 2n$ (i.e. 200, 110, etc.). This shows that the centres of the scattering molecules are separated by a distance $R(x, y, z)$ with $x = a/2$ and $y = b/2$. Consequently, two chains pass through the unit cell of cellulose, one of which is the "angular" chain with the coordinates $(0, 0, z)$, and the other is the "central" chain with the coordinates $(1/2, 1/2, z)$. Two versions of the arrangement of chains are then possible. In the first the chains occupy common positions and are linked by a screw axis in the $(1/4, 1/4, z)$ position. In this case the symmetrically independent unit of the crystal and the repeat unit of the polymer chain consists of a cellobiose fragment, the chains have the same direction (are parallel), and are displaced relative to one another by half the translation along the c axis. In the second version, the chain structures are located on the 2_1 screw axes, are crystallographically non-equivalent, and can be both parallel and anti-parallel. The symmetrically independent unit of the crystal consists of a pair of glucose residues (one in each chain); the repeat unit is also a glucose residue.

The choice between the above two versions of the structure is made on the basis of the intensity of the meridional 002 and 004 reflections. In the first version of the packing, the centres of the glucose units are displaced by $c/2$ along the z axis. For this version, the 002 reflection should be more intense than the 004 reflection, which conflicts with experiment. In the second version of the structure, the displacement of the glucose rings of the neighbouring chains is arbitrary and there are no limitations as regards the ratio of the intensities of the 002 and 004 reflections.

Thus the unit cell of cellulose, constructed on the basis of X-ray diffraction data, has the space group $P2_1$ (monoclinic system) and contains two crystallographically non-equivalent chains intersecting the ab plane at the origin of coordinates and at the centre. The symmetrically independent unit of each cell is the glucopyranose residue. In order to account for the observed intensity ratio of the even meridional reflections, it is usually assumed that the central chain in the two-chain unit cell is displaced by approximately $c/4$ relative to the angular chain.

The repeat period along the axis of the cellulose fibre, calculated from the distance between the meridional reflections on the X-ray diffraction pattern, is approximately 10.3 Å. The remaining unit cell parameters are found by indexing the diffraction patterns. Wellard[26,27] first drew attention to the fact that, even within the framework of a single polymorphic modification of cellulose, the unit cell parameters are within a fairly wide range. For example, the parameter a in CI varies within the limits 8.17–8.35 Å, the parameter b within the limits 7.78–7.90 Å, and the monoclinic angle γ in the range 96.0–96.5°. In CII the ranges of variation of the parameters are even greater: 7.83–8.14 Å for a, 8.99–9.38 Å for b, and 116.6–118° for γ. It is believed[3] that celluloses of different origin do indeed have different unit cells. The unit cell parameters depend on the content of impurities, the defectiveness of the crystallites, the heterounit nature of the polymer chain, and other factors, which can be determined to a large extent by the methods used to isolate and purify cellulose.

The model of the cellulose unit cell described above has been frequently criticised. Thus a number of workers[28–30] observed weak odd meridional $00l$ reflections, which cast doubt on the presence of the 2_1 axis in the structure. Special studies have shown, however, that these reflections are very weak and may be accounted for by the overlapping of neighbouring reflections.[31,32]

Norman[32] and Kitaigorodskii[34] drew attention to the fact that the appearance of odd meridional reflections may be a consequence of one-dimensional diffraction. However, one-dimensional diffraction calculations for the third layer line yielded an appreciably smaller intensity (by approximately 30%) than its observed value. According to Kitaigorodskii and Tsvankin,[33,34] cellulose nevertheless possesses a screw axis symmetry and the differences between the calculated and observed intensities can be associated with structural defects.

A simple model of the defects in the crystal structure of cellulose has been examined by Stipanovic and Sarko,[35] who suggested, as regards the calculation of the theoretical intensities, that the hydroxymethyl groups of the neighbouring residues in the chain are in different positions linked to one another by 120° rotation. However, the theoretical intensities of the 001 and 003 reflections, calculated for the given disordered model, proved to be much higher than the observed values, which permitted the conclusion that, even if orientational disorder of this kind is present in the cellulose structure, it involves only very few chains, for example, the chains located on the surfaces of crystallites.

Apart from diffraction data, NMR and IR spectroscopic data have been invoked for the discussion of the model of the cellulose unit cell described at the beginning of this Section. Thus the splitting of the signals due to the C(1) and C(4) atoms has been observed in the high resolution NMR spectrum of solid cellulose.[36,37] These two well resolved doublets indicated the presence in cellulose of symmetrically different pairs of C(1) and C(4) atoms and were interpreted as proof of the absence of the 2_1 screw axis from cellulose. An analogous situation obtained also in the study of the IR spectra,[38] where the bands with parallel dichroism at 3448 and 3488 cm^{-1} were attributed to two non-equivalent O(3)H...O(5′) hydrogen bonds alternating along the axis of the cellulose macromolecule.

The use of the above experimental facts as proof that the cellulose chain is not a helix with 2_1 symmetry constitutes in our view a misunderstanding. As noted above, the cellulose unit cell, constructed using the X-ray diffraction data, includes two crystallographically non-equivalent chains. In these chains the C(1) and C(4) atoms can have different local environments just as the O(3)H...O(5′) hydrogen bonds can have different structures. These differences are fully capable of giving rise to the difference in the NMR and IR spectra, so that their interpretation does not in any way make it necessary to "deprive" the cellulose chain of 2_1 symmetry.

In discussing the two-chain model of the cellulose unit cell with $P2_1$ symmetry, it is necessary to mention separately the structural studies of certain specific varieties of natural cellulose. Thus the X-ray diffraction patterns of seaweed[28,39] (*Valonia ventricosa*, *Chaetomorpha*) were found to contain three weak reflections (d = 8.61 and 4.42 Å along the first layer line and d = 3.29 Å along the third), which are absent from the X-ray diffraction patterns of cotton, ramie, flax, and wood cellulose. These reflections cannot be indexed on the basis of a two-chain unit cell model and require the doubling of the parameters a and b, which formally leads to models with eight crystallographically non-equivalent chains per unit cell. It may be that such non-equivalence of the chains in the increased cell reduces to a simple shift of the neighbouring chains relative to one another by $c/4$ along the axis of the fibre.[40,41]

Yet another feature of the cellulose from seaweed was observed in an electron diffraction study of specimens with biaxial surface orientation.[29,30] It was found that the intensities of certain *hkl* and $\bar{h}\bar{k}l$ reflections do not coincide, which requires the reduction of this symmetry to triclinic.

Despite the fact that the electron diffraction data[29,30] are not entirely convincing (owing to the strong dependence of the intensity of the reflections on the orientation of the reflecting planes), it should probably be recognised that cellulose from seaweed can indeed have an "individual" unit cell.

2. Conformation of the Monomer Unit

Whereas the symmetry and size of the cellulose unit cell have been determined by direct experimental studies, unfortunately only indirect data are available as regards the conformation of the monomer unit of cellulose. These are in the first place X-ray diffraction data for crystals of low-molecular-weight sugars and carbohydrates and also the results of theoretical conformational analysis.

It has been established experimentally and theoretically[18–21,42–47] that β-D-glucose, which is the elementary unit of the cellulose helix, has the "chair" form and is in the C1 conformation in terms of Reeves' nomenclature.[48–50] Three independent X-ray diffraction studies of β-cellobiose[51–53] showed that the conformation of its monomer units corresponds to the C1 form. Arnott and Scott[54] analysed the X-ray diffraction studies of the single crystals of low-molecular-weight sugars and carbohydrates. Statistical analysis of 27 model compounds, whose monomer unit is a pyranose ring (among these, 17 compounds contained a glucopyranose ring), showed that they all have the C1 conformation. The standard deviations of the geometrical parameters of the ring from the corresponding average values are extremely insignificant, which indicates a high conformational rigidity of the pyranose rings.

Conformational analysis of D-aldopyranoses, carried out by Rao and co-workers[55,56] and then in other investigations,[18,45–47] showed that, whatever the spatial disposition of the side groups, the C1 form is preferable on energy grounds and the ring geometry depends only slightly on the perturbing influence of the side groups. The valence angles at the carbon atoms remain close to the tetrahedral value and the angle at the oxygen ring atom is 112–114°. We may note that the ring conformation remains unaltered even in the presence of bulky substituents such as the nitrate groups.[57]

3. The Conformation of the Cellulose Helix

Bearing in mind the high conformational rigidity of the glucopyranose ring and also the constancy of the valence bonds and angles in the side groups, one may assume that the model of the cellulose chain which permits the variation of only the orientations of the side groups and of the parameters of the junction of the monomer units is fully acceptable. The valence angle β of the glucosidic oxygen atom (Fig.2) and also the torsional angles ϕ and ψ for the rotation of the monomer units about the C(1)–O(1) and O(4)–C(4′) bonds are usually employed to describe the geometry of the junction of the monomer units. The angles ϕ and ψ are determined by the sets of four atoms H(1)–C(1)–O(1)–C(4′) and C(1)–O(4)–C(4′)–H(4′) respectively.

The angles β, ϕ, and ψ are extremely convenient for the description of the geometry of the junction, since they make it possible to use standard computer programs for conformational analysis in order to generate the fragments of the cellulose macromolecule. At the same time, the parameters ϕ, ψ, and β suffer from a significant disadvantage, namely the cellulose chain does not meet the symmetry requirements for their arbitrary values. In other words, in generating the model of the cellulose chain with the aid of the above parameters, one cannot make use of the experimental fact that the cellulose chain is a helix with 2_1 symmetry.

Yet another experimental result, which cannot be used to describe the junction of the monomer units in terms of the angles ϕ, ψ, and β is the fact that the repeat period of the cellulose chain is approximately 10.3 Å and remains the same in all the polymorphic modifications of cellulose.[7–11]

It is easy to show that, for the specified conformation of the monomer unit and symmetry of the helix (2_1), only two parameters are needed to describe the conformation of the main chains. It has been suggested that the angle δ, determining the rotation of the monomer unit about the virtual O(4)...O(4′) bond, and the angle ε, determining the slope of this virtual bond relative to the axis of the helix (Fig.2), be used as such parameters.[58,59] The idea of switching to parameters describing the junction of not real but virtual bonds was developed in the so called variable virtual bond method.[60,61] The independent conformational parameters of the main chain are the angle δ and the half-period $c/2$ (or h), while the conformational parameters of the junction (ϕ, ψ, and β) are dependent variables. This algorithm is applicable to molecules with any structure of the main chain provided that its symmetry is known.

Passing now to the determination of the parameters specifying the orientation of the side groups in the cellulose chain, we may note immediately that in the vast majority of structural

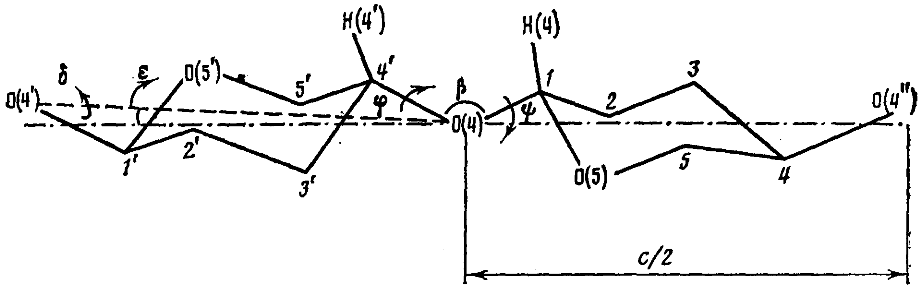

Figure 2. The structural parameters used to describe the conformation of the main chain of the macromolecule.

studies on cellulose hydrogen atoms are disregarded.[28,35,62-64] In this case it is sufficient to introduce only one angle, describing the rotation of the hydroxymethyl group about the C(5)–C(6) bond. The following designations have been adopted for the description of the position of the hydroxymethyl group:[65]

(a) *gt*—*gauche*-position of the C(6)–O(6) bond relative to the C(5)–O(5) bond and *trans*-position relative to the C(4)–C(5) bond;

(b) *tg*–*trans*-position of the C(6)–O(6) bond relative to the C(5)–O(5) bond and *gauche*-position relative to the C(4)–C(5) bond;

(c) *gg*—*gauche*-position relative to both bonds.

A number of investigators believe[36] that the *gt*-orientation of the CH_2OH group is most probable for cellulose chains, because this conformation is typical of crystalline monosaccharides[46,47,66] and certain oligosaccharides.[51-53,67,68] However, experimental data for cellotetraose[69,70] agree best with the hypothesis of the *tg*-conformation of the hydroxymethyl group.

In the entire set of parameters describing the conformation of the cellulose chain, the angle β at the glucosidic oxygen atom has been most reliably determined. According to the statistics of Arnott and Scott,[54] β varies in the range 115.7 to 117.6° in model compounds whose monomer unit is the glucopyranose ring. This range can be adopted as the most probable range of variation of the angle β.

In the early structural models of cellulose, proposed by Meyer and co-workers,[71,72] the angle β was assumed to be 109° and the torsional angles ϕ and ψ were assumed to be zero. (The conformation of the chain with $\phi=\psi=0°$ is usually referred to as the "straight" conformation, in which the plane of the glucosidic bonds is perpendicular to the plane of the glucopyranose ring). The hydroxymethyl group is close to the *tg*-position. For this set of parameters, there are no intermolecular hydrogen bonds in the system. The straight conformation can hardly be regarded as acceptable owing to the presence of certain short non-valence contacts between successive units [in particular the distance between the H(1) and H(4) atoms is 1.7 Å].

The so called "bent" conformation of Hermans et al.[73] is more realistic. This conformation can be obtained from the straight conformation by the rotation of the monomer units about the C(1)–O(1) and O(4)–C(4) bonds by angles of approximately 25°. In the bent conformation there are no shortened non-valence contacts and the distance between the O(3) and C(5′) atoms in successive units is close to 2.7 Å, which indicates the possibility of the formation of the O(3)H...O(5′) intramolecular hydrogen bond. We may note that in crystalline cellobiose[51-53] the relative positions of the glucopyranose rings correspond precisely to the "bent" conformation with its characteristic O(3)H...O(5′) hydrogen bond.

In the structural studies mentioned above,[58,59] the optimum conformation of the β-D-(1 → 4)-linked residues is also close to the bent conformation. It has been shown that reasonable values of δ (which do not lead to short non-valence contacts on either side of the oxygen bridge) are in a narrow range, where there is a possibility of the formation of the O(3)...O(5′) hydrogen bond.

Conformational analysis of the β-D-glucose residues linked in different ways to give a dimeric fragment (linkages of the 1 → 2, 1 → 3, and 1 → 4 types) has been carried out[56] within the framework of the semiempirical model of molecular mechanics.[21] The potential energy of the system, including the energy of the non-valence interactions and the energy of the hydrogen bonds, was calculated as a function of two angles, ϕ and ψ, for the fixed angle $\beta = 117.5°$. The calculations showed that the global minimum of the potential energy of the (1 → 4)-linked dimer is close to the conformation corresponding to the 2_1 symmetry. Furthermore, it has been established that only 4% of the space of the changing variables does not lead to short covalent contacts between the atoms in successive units. This agreed qualitatively with the results of the calculations by Jones[58] and confirmed the view of Rees and co-workers[74,75] that cellulose chains are highly rigid.

In the analogous conformation calculations by Sarko and Muggli,[28] the potential energy of the system was recorded as the sum of the squares of the deviations of the geometrical parameters of the structure from standard values. Analysis of the ϕ–ψ map showed that the conformation of the chain with the *tg*- and *gt*-orientations of the O(6) atom, corresponding to the 2_1 conformation and a repeat unit of 10.3 Å, is close to the potential energy minimum. In the case of the *tg*-orientation, there is a possibility of the formation of the O(2)H...O(6′) bond on the other side of the oxygen bridge in addition to the O(3)H...O(5′) hydrogen bond.

Panov et al.[76] included the energies of the non-valence and electrostatic interactions, the torsional potentials, and the energy of the hydrogen bonds in the conformational energy of the dimeric cellulose chain fragment. The angle β was assumed to be 116.0°. The conformation with the *tg*-orientation of the hydroxymethyl group and the parameters ϕ and ψ corresponding to the 2_1 symmetry proved to be most preferred as regards energy. Two hydrogen bonds, O(3)H...O(5′) and O(2)H...O(5′), were present in the system and according to the authors only these bonds can be formed simultaneously. The conformations with hydrogen bonds of the type O(6)H...O(2′) and O(6)...O(1′) are less favourable as regards energy.

A more detailed analysis of the conformational possibilities in the cellulose macromolecule has been carried out recently.[61] The method of the variable virtual bond is used in constructing the main chain, since the search for the optimum chain conformation was restricted *a priori* by the subset of conformations satisfying the helical 2_1 symmetry. The conformational energy included the energy of the atom–atom non-valence interactions, the torsional contributions, the deformation energy of the angle β, and the potentials of the hydrogen bonds. In order to discover the regions of the permissible conformations of the main chain, a preliminary calculation was carried out in which the pitch of the helix was assumed to be constant and the angle δ was varied from −180° to 180°. It is seen from Fig.3 that two comparatively narrow regions correspond to reasonable values of the angle β ($114 \leq \beta \leq 118°$): $44° \leq \delta \leq 58°$ and $-70° \leq \delta \leq -56°$. The same Figure presents the dependence of the O(2)...C(6′) distance on the angle δ. Evidently the range $-70° \leq \delta \leq -56°$ can be eliminated from consideration with full justification owing to the presence of unduly short O(2)...C(6′) contacts. Subsequent calculations by Pertsin et al.[61] consisted in minimising the conformational energy in the space of six changing variables. The variables included four tortional angles $\tau_i (i = 1, \ldots, 4)$, confirming the orientation of the side groups, the angle δ, and the pitch of the helix *h*. The calculations revealed the six stable conformations of the isolated cellulose helix. These conformers are designated in Figs.4–6 by *A*1, *A*2, *B*1, *B*2, *C*1, and *C*2. Their conformational energies were −4.8, 3.1, 0.3, −0.5, −0.1, and 2.6 kcal mol^{-1} respectively.

Evidently all the stable conformers of the isolated helix are characterised by the presence of the O(3)H...O(5′) bond. As mentioned above, the presence of bonds of this kind has been confirmed by numerous experimental findings. In the conformer *A*1, which is most preferred as regards energy, there is also the O(4)...O(6)H...O(2′) hydrogen bond, which includes one donor and two acceptor oxygen atoms. The possibility of the formation of such bonds has been recently demonstrated by a non-empirical quantum-chemical calculation[77,78] and by a neutron diffraction study of carbohydrate crystals.[79,80] (Bonds of this type will henceforth be referred to as a biacceptor in contrast to the bidonor bonds of the type OH...O...HO).

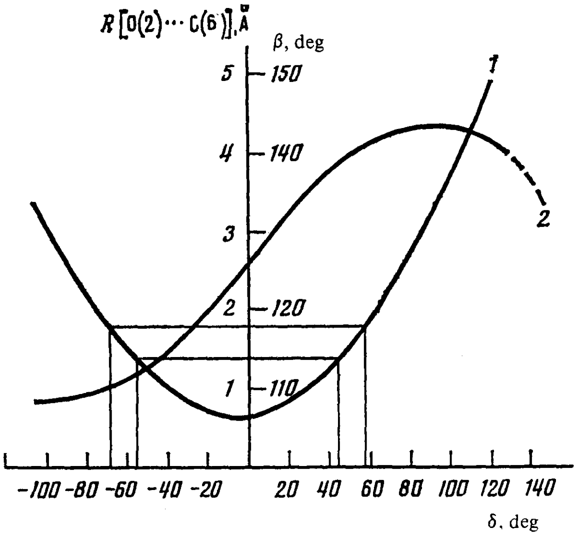

Figure 3. The permissible ranges of variation of the angles δ:[61] 1) dependence of β on δ; 2) dependence of the interatomic O(2)...C(6') distance on δ.

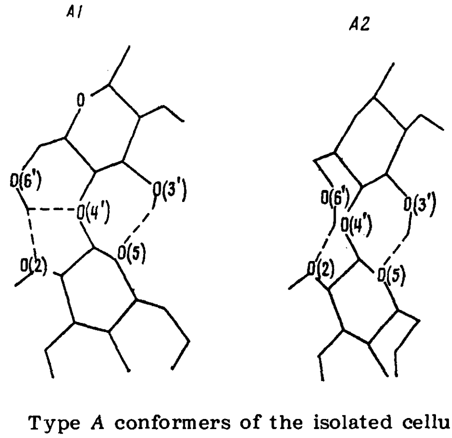

Figure 4. Type *A* conformers of the isolated cellulose helix. (Here and henceforth the hydrogen bonds are shown by dashed lines; for clarity, the ring hydrogen atoms are not shown).[61]

The hydroxymethyl group of the conformer *A*1 is close to the *tg*-position ($\tau_1 = 60°$). The rotation of this group by approximately 83° brings the hydroxymethyl group closer to the *gg*-position ($\tau_1 = -60°$) and affords the new stable conformer *A*2 (Fig.4). The bond O(6)H...O(4) is then broken and only the usual O(6)H...O(2') hydrogen bond remains. The O(6)...O(2') hydrogen bond can be formed also via the proton at the O(2) atom, which becomes the donor, and the O(6) atom—the proton acceptor. The situation described is characteristic of conformers of type *B* (Fig.5), which constitutes their principal difference from type *A* conformers. As for type *A* conformers, there is a possibility of two different positions of the hydroxymethyl group leading to the formation of the O(2)H...O(6') bond. In the conformer *B*1, the orientation of the O(6) atom is close to the *tg*-position, while in the conformer *B*2 it is close to the *gg*-position.

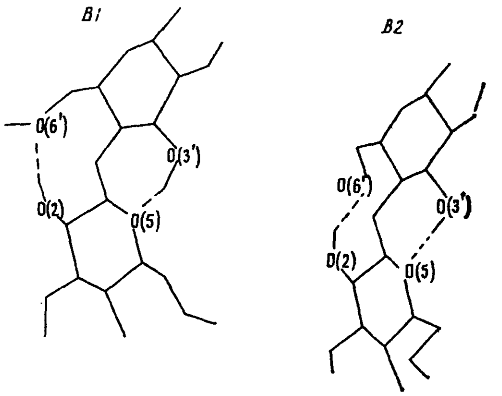

Figure 5. Type *B* conformers of the isolated cellulose helix.

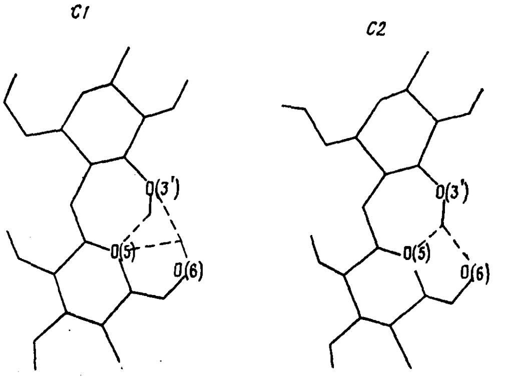

Figure 6. Type *C* conformers of the isolated cellulose helix.

It is seen from Fig.6 that there are also two stable *C*1 and *C*2 conformers whose hydroxymethyl groups are close to the *gt*-position ($\gamma_1 = 180°$). The biacceptor O(3')...O(6)H...O(5') bond and the bidonor O(6)H...O(5)...HO(3') bond are present in the conformer *C*1. In the conformer *C*2, whose energy is smaller than that of the conformer *C*1 by approximately 2.7 kcal mol^{-1}, only the biacceptor bond of the type O(5')...O(3)H...O(6') is present.

All six stable conformers of the isolated cellulose helix have an equilibrium period close to the observed repeat period (approximately 10.3 Å). The equilibrium values of the angle β are also close to those in carbohydrates and polysaccharides (115.7–117.6°). Furthermore in all the conformers there are vacant sites for the formation of intermolecular hydrogen bonds. For this reason, each of the conformers found can in principle exist in the crystal.

The results of the conformational analysis reveal extremely extensive conformational possibilities in the cellulose macromolecule, indicating thereby the impossibility of an unambiguous prediction of its crystal structure from the consideration of an isolated chain. Evidently the packing of the macromolecules in the crystal and, in particular, the formation of intermolecular hydrogen bonds can affect significantly the relative stabilities of particular conformers.

III. STRUCTURAL MODELS OF THE MAIN POLYMORPHIC VARIETIES OF CELLULOSE

In describing the crystal structure of cellulose, the following packing parameters are usually employed: two angles of rotation of the chains about their bonds, the shift of the chains relative to one another, and two parameters specifying the direction of the chains. Here and henceforth we shall adhere to the following notation: the angles of rotation ϕ^k of the angular ($k = 1$) and central ($k = 2$) chains, the shift S of the O(4) atom of the central chain relative to the O(4) atom of the angular chain along the c axis (in fractions of the period c), and the directional parameter $p^k = \pm 1$ ($p^k = \pm 1$ if $z_{O(5)} \gtrless z_{C(5)}$ for the kth chain).

1. Cellulose I

As already mentioned, natural celluloses of different origin, for example, from cotton, flax, hemp, ramie, wood, etc., belong to this polymorphic modification.

The first X-ray diffraction studies on flax and hemp celluloses were carried out ten years before it was established that cellulose is a glucose polymer. At the end of the 1920's and 1930's, the familiar structural studies by Meyer and Mark,[71] Meyer and Misch,[72] Pierce,[83,84] etc. were published. These have played a decisive role in the development of ideas about the structure of crystalline regions of cellulose. Among the early structural investigations, we may also include the studies by Frey-Wyssling,[85] Marrinan and Maan,[86,87] Liang and Marchessault,[88,89] etc. carried out during the period between the 1940's and 1960's.

At the present time most of the early studies are of purely historical interest, because the structural models proposed in them conflict with later experimental data.

Thus it was assumed in Pierce's model[83,84] that the glucopyranose ring is in a planar conformation, which conflicts with experimental data considered in Section II. In Frey-Wyssling's model,[85] there is a free hydroxyl at C(2), which conflicts with IR spectroscopic data,[9,15,45,90] according to which all the hydroxy-groups of cellulose are involved in hydrogen bonds. Many early structural models, in particular the well known model of Meyer and Misch,[72] to not agree with data for the IR dichroism of the stretching vibrations of the OH groups. According to these data, in the region of such stretching vibrations[9,15,90] there are five bands, of which two exhibit perpendicular dichroism while the remaining exhibit parallel dichroism. This shows that there should be at least two OH groups in solid cellulose with preferential perpendicular orientation relative to the axis of the fibre and at least three OH groups with preferred parallel orientation. In Meyer and Misch's model mentioned above,[72] there are only intermolecular hydrogen bonds with preferential perpendicular orientation, i.e. the existence of three bands with parallel dichroism could not be accounted for in terms of this model.

Of the structural models belonging to the end of the 1960's, mention should be made of those of Maan and Marrinan[86] and Liang and Marchessault.[88] Maan and Marrinan's models were based mainly on the IR dichroism data mentioned above. X-Ray diffraction data were scarcely taken into account in these models (with the exception of the unit cell parameters). In the analysis of the structure of cellulose, Liang and Marchessault[88,89] combined spectroscopic data with the intensities of well resolved reflections. All the models proposed by the authors agreed satisfactorily only with the IR dichroism of the OH groups but conflicted with X-ray diffraction data.[58,59]

The first serious attempt to reconcile the stereochemical, IR spectroscopic, and X-ray diffraction data was undertaken by Jones.[58,59] Seven alternative CI models, differing in the relative polarities of the chains, the rotation of the monomer unit about the virtual O(4)...O(4′) bond, and the orientation of the hydroxymethyl group and the chains in the unit cell were considered. All the models considered satisfied the stereochemical criteria and agreed with IR spectroscopic data. The best agreement could be observed in X-ray reflection intensities (among the models examined) obtained for the antiparallel model, whose parameters are close to those of the modern structural models of CI.

The Jones model includes two intramolecular bonds, O(3)...O(5′) and O(2)...O(6′) [The orientation of the O(6) atom is close to *tg*] and the intermolecular O(6)...O(3″) bond located in the (200) plane. The chains are uncoiled around their axes in such a way that the planes of the glucopyranose rings are arranged almost parallel to the *ac* plane, forming a layered structure. The O(6)...O(3″) bond forms translationally identical chains, i.e. is located within the layer. The main difference between the Jones model described and the earlier structural models is the absence of interlamellar hydrogen bonds (between the angular and central chains).

As regards the structural model proposed by Jones for CI,[58] mention should be made that it has not been optimised in the sense that it does not correspond to the optimum of any specific criterion in the space of the changing variables. In essence, the Jones model is only the best among the seven discrete models examined by the author.

The search for the structural models of cellulose was first reduced to the optimisation problem in a study by Gardner and Blackwell.[91] The crystallographic divergence factor (R factor) was adopted as the target optimisation function:

$$R = \sum_{m=1}^{M} \Delta F_m / \sum_{m=1}^{M} |F_{m(\mathrm{obs})}| \qquad (1)$$

where $\Delta F_m = |F_{m(\mathrm{obs})} - F_{m(\mathrm{calc.})}|$ and the F_m are structural amplitudes. The summation in Eqn.(1) is carried out with respect to M observed reflections. The calculated structural amplitudes were obtained from the formula

$$F_{m\,(\mathrm{calc})} = K \left\{ \sum_{hkl} [F^{hkl}_{m\,(\mathrm{calc})} \exp(-B_T d_m^2/4)]^2 \right\}^{1/2} \qquad (2)$$

where K is the scaling factor, B_T the average isotropic temperature factor, and d_m the interplanar distance in the inverse lattice. The summation in Eqn.(2) is carried out with respect to all the hkl planes contributing to the mth reflection.

By comparing alternative models, Gardner and Blackwell[91] also calculated weighted R factors:

$$R' = \sum_{m=1}^{M} w_m^{1/2} \Delta F_m / \sum_{m=1}^{M} w_m^{1/2} |F_{m\,(\mathrm{obs})}| \qquad (3)$$

$$R'' = \left\{ \sum_{m=1}^{M} w_m \Delta F_m^2 / \sum_{m=1}^{M} w_m F^2_{m\,(\mathrm{obs})} \right\}^{1/2} \qquad (4)$$

where w_m are the weighting factors:

$$\Delta F_m^2 = |F_{m\,(\mathrm{obs})}^2 - F_{m\,(\mathrm{calc})}^2|.$$

In contrast to Eqn.(2), the summation in Eqns.(3) and (4) is carried out not only with respect to the observed reflections but also with respect to the postulated refelctions. The postulated reflections are included in the calculation of the R factor in order to avoid the appearance of intense theoretical reflections for planes which are not observed experimentally. The experimental set of values of $|F_m(\mathrm{obs})|$ was obtained on fibres from *Vallonia ventricosa.* The meridional $00l$ reflections were not included in the calculation of the R factor because of certain difficulties associated with the measurement of their intensities and the introduction of the Lorentz and polarisation corrections.

In the search for the most preferred structure of CI, the following initial trial models were employed;[91]

(1) P_1—parallel chains ($p^1 = p^2 = 1$), $S = {}^1/_4$;
(2) P_2—parallel chains ($p^1 = p^2 = -1$), $S = {}^1/_4$;
(3) a_1—antiparallel chains ($p^1 = 1$, $p^2 = -1$), $S = -{}^1/_4$;
(4) a_2—antiparallel chains, $S = {}^1/_4$.

In constructing the cellulose helix, the bond lengths and valence angles were set equal to their standard values.[54] The conformation of the main chain was assumed beforehand to be that corresponding to the helical symmetry 2_1 and the repeat period 10.38 Å and was not varied in the course of the calculations. The parameters of the junction of the monomer units were assumed to be equal to the values for which the O(3)...O(5′) hydrogen bond may be formed between the O(3) and O(5′) atoms ($\phi = 23°$, $\psi = -27.7°$, $\beta = 144.8°$).[56]

The optimum model was sought in the space of six changing variables.[91] These included the angle τ_1, describing the rotation of the hydroxymethyl groups (in both chains simultaneously), the three packing parameters ϕ^1, ϕ^2, and S, and also the parameters B_T and K which occur in the formulae for the calculation of the structural amplitudes [Eqns.(2)].

The model obtained from the P_1 approximation ($R = 0.254$, $R' = 0.233$, $R'' = 0.215$, and $B_T = 2.5$ Å^2) was found to be best. The shift in the optimised P_1 model was $S = 0.266$. In these models the intermolecular O(6)...O(3″) hydrogen bond is located in the (020) plane. In addition to the O(3)...O(5′) intramolecular bond, whose presence is predetermined by the initial chain conformation, the O(2)H...O(6′) bonds arises on the other side of the oxygen bridge. This bond is formed when the O(6) atom is located in a position differing from *tg* by 20°. The values of τ_1 corresponding exactly to *tg*, *gt*, and *gg* are found to be stereochemically unsuitable in the crystal and give rise to high values of the R'' factor (0.24, 0.29, and 0.35 respectively).[91]

The assumption by Gardner and Blackwell of the absolute rigidity of the main chain of the macromolecule can apparently be regarded as the main disadvantage of their treatment,[91] because the monomer units of cellulose exhibit a definite freedom of rotation about the virtual bonds. The neglect of this rotation can significantly impair the "packing possibilities" of the cellulose chains. In particular, the packing of rigid chains can lead to shortened contacts, which might have been avoided by means of small changes in the conformation of the main chain.

Among the disadvantages of the treatment of Gardner and Blackwell,[91] one should include also the fact that, in selecting the initial approximations, the authors, considered only two discrete values of the parameter $S(\pm{}^1/_4)$, leaving uninvestigated most of the range of variation of this parameter. Here it is appropriate to mention that the values $S = \pm{}^1/_4$ arise from the intensity of the 002 and 004 reflections only if we assume that the scattering centres of the cellulose chain are concentrated at the centres of the glucopyranose rings. The above approximation is fairly rough and, as will be shown below, the observed intensity ratios of the four meridional reflections can be obtained for values of S extremely remote from $\pm{}^1/_4$.

A more complex method for the refinement and selection of the optimum cellulose model was adopted by Sarko and co-workers.[28,93] The optimum model was determined by minimising a target function Φ of the following type:

$$\Phi = 100fR'' + (1-f)Y \tag{5}$$

where $f = 0.8$ is the weighting factor and Y is the sum of the standard deviation functions taking into account the deviation of the geometrical parameters of the model from their standard values.[93] In the calculation of the R'' factor, the authors used in Eqn.(5) the X-ray diffraction data obtained using ramie fibres.

In order to test the hypothesis that the 2_1 axis is present in the crystal structure of cellulose, the authors[28,93] eliminated the limitations associated with the $P2_1$ symmetry and varied all the geometrical parameters of the model with the exception of their bond lengths (23 parameters in all). Apart from the geometrical parameters, the average temperature multiplier was also varied, being assumed to be anisotropic in the given instance and having three dependent components.

Two structural models were found to be most suitable as regards the value of Φ. These are a model with parallel packing of the chains ($R'' = 0.193$) and the antiparallel model ($R'' = 0.246$). In both cases the deviations from the symmetry of the 2_1 screw axis were found to be insignificant and did not exceed 1–2° for the valence and torsional angles in the ring and in the junction of the monomer units. In order to discover the best models, the authors resorted to Hamilton's statistical tests.[92] If a one-dimensional hypothesis is assumed (i.e. that either the parallel or the antiparallel model is possible), then the differences in the R' factor for the fifty observed reflections supporting the parallel model are found to be significant at a level of significance of 99.5%.

In terms of its structural parameters and especially the system of hydrogen bonds, the model proposed by Sarko and co-workers[93] proved to be close to the P_1 model of Gardner and Blackwell.[91] In assessing the method used by Sarko and co-workers[28,35,60,62,93] for the elucidation of the cellulose structure, it is necessary to note the following points. Firstly, the inclusion in the optimisation of "rigid" variables such as the valence angles and bond lengths has little justification.[35,62] The variation of these variables usually sharply impairs the convergence of the optimisation process, so that the target function becomes sensitive mainly to the "rigid" variables. The search for the optimum values of the "sensitive" parameters (torsional angles, the rotations of the chains, etc.) becomes greatly hindered owing to the oscillations in the "rigid" variables about their equilibrium values.

Yet another disadvantage of the method of Sarko and co-workers[93] is the absence, in an explicit form, of terms describing hydrogen bonds in the target function (5). For this reason, the endeavour by the system to achieve the maximum saturation by hydrogen bonds is not reflected in the optimisation of the target function.

Finally, it is essential to note also the serious error which Woodcock and Sarko[93] made in applying Hamilton's tests to the comparison of the best parallel (P) and antiparallel (a) models. As already stated, in determining the significance of the differences in the R'' factors between the a and P models, the authors assumed a one-dimensional hypothesis. This would evidently be correct if the a and P models differed only by the relative chain polarities. In reality the a and P models differ also by all the remaining parameters, whose number (23) actually determines the dimensions of the hypothesis. If the dimensions of the hypothesis are assumed to be 23, then the a and P models are found to be statistically indistinguishable whatever the level of significance.

The insolubility of the problem of the relative chain polarities in CI was yet again demonstrated in French's study.[94] This was the best founded and interesting crystallographic investigation of CI based on thoroughly analysed and corrected experimental data (obtained from ramie cellulose) and a well balanced computational model.

As regards the experimental part of the study, the author was able to determine for the first time the intensities of the meridional 002 and 004 reflections, which proved to be extremely significant in finding the orientation of the hydroxymethyl group. From the standpoint of the selection of the changing variables, French's computational model occupies an intermediate position between the model of Gardner and Blackwell and the model of Sarko and co-workers. On the one hand, French's model is free from the defects of Gardner and Blackwell's model, since it assumes the deformation of the main macromolecular chain (as a result of the rotation of the monomer units about the virtual bond). On the other hand, in contrast to the model of Sarko and co-workers, in French's model there are no "rigid" parameters, since all the bond lengths and valence angles are assumed to be constant in the course of the solution of the structural problems (with the exception of the valence angle at the glucosidic oxygen atom).

Altogether French's computational model included nine changing variables, among which were the angles τ_1^k, ϕ^k, and δ^k as well as the parameters p^k and S described previously. Initially French[94] assumed different values of τ_1^k and δ^k in the angular and central chains and also in two successive monomer residues, but this proved to be superfluous; neither the abandonment of the 2_1 symmetry nor the introduction of conformational differences between the angular and central chains entailed an appreciable improvement of the R'' factor.

The antiparallel model ($R'' = 0.158$), designated by the author[94] as the a_1 model, proved to be most suitable as regards the R'' factor. In this model, the macromolecules are linked into layers by intermolecular O(6)...O(3″) hydrogen bonds. Apart from the O(3)...O(5′) intramolecular bond, when the position of the O(6) atom is close to *tg*, there is a possibility of the formation of two hydrogen bonds of the type O(2)...O(6′) and O(6)...O(4). The existence of the latter bond is extremely doubtful according to French,[94] since it differs markedly from the linear bond and in addition the bridging O(4) oxygen atom is a weak proton acceptor.

The best "parallel" models found by French (the P_1 and P_2 models) differed very insignificantly from the a_1 model as regards the value of the R'' factor ($R''_{P_1} = 0.185$ and $R''_{P_2} = 0.175$). This made it impossible for the author[94] to reach the unambiguous conclusion that the packing of the chains in CI is antiparallel. Application of Hamilton's test[92] shows that the hypothesis of the parallel disposition of the chains in CI can be rejected only for an extremely low level of significance (95.0%).

The difficulties arising in the interpretation of the diffraction data for cellulose made it necessary to resort to non-crystallographic criteria, in particular to the energy criterion. Thus Nugmanov and co-workers[95,96] sought the structure of CI by optimising a target function of the type

$$\Phi = U + \omega R'' \qquad (6)$$

where U is the potential energy of the system and ω the weighting factor chosen to ensure that the maximum statistically insignificant changes in U and R'' make identical contributions to Φ ($\omega = 15$ kcal mol^{-1}). The potential U was calculated by the method of atom–atom potentials;[20,96,97,98] it included both intramolecular and intermolecular components. The optimum structure was sought in the space of 16 variable parameters: τ_i^k, δ^k, ϕ^k, S, p^k, and B_T.

A considerable number of local minima in the target function were discovered in the course of the calculations.[95] The characteristics of the deepest of these are presented in Table 1. The fact that the values of the R'' factor for the best structural model lie within the comparatively narrow range 0.24–0.16 is striking when Table 1 is analysed. Application of Hamilton's statistical test[92] shows that, for the usual 99% level of significance, the vast majority of the models considered (with the exception of the a_3 and a_4 models) are statistically equivalent. This illustrates clearly yet again the ambiguity of the solution of the structural problem for CI on the basis of the available diffraction data even when stereochemical packing limitations are introduced.

Table 1. Certain characteristics of the most probably structural models of CI.[95,96]

Model*	R''	U, kcal mol^{-1}	Φ, kcal mol^{-1}	Model*	R''	U, kcal mol^{-1}	Φ, kcal mol^{-1}
$\bar{P}_1$	0.165	−19.9	−17.4	a_1	0.213	19.7	−16.5
$\bar{P}_2$	0.187	−19.7	−16.9	a_2	0.155	−18.6	−16.1
$\bar{P}_3$	0.182	−17.9	−15.2	a_3	0.240	−19.7	−16.0
P_1	0.167	−17.5	−14.6	a_4	0.240	−19.7	−16.0

*The parallel models, designated by P_i and $\bar{P}_i$, correspond to the "average" polarity $p = (p^1 + p^2)/2 = \pm 1$, while the antiparallel a_i models correspond to the polarity $p = 0$.

It is significant that, in the course of the search for a global minimum in the target function Φ,[95] many structural models proposed previously for CI were discovered. Thus the models designated in Table 1 by P_1 and a_3 respectively are analogues of the Gardner–Blackwell–Sarko[64,93] and French[94] models just considered above. Here the analogy is manifested both by the similarity of the geometrical parameters of the models and by the complete identity of the hydrogen bond systems. Evidently the P_1 and a_2 models are not best as regards either the energetic standpoint or as regards the value of the R'' factor.

The global minimum in the target function was found within the framework of a parallel arrangement of the chains whose direction was opposite to that in the P_1 model (the $\bar{P}_1$ minimum in Table 1). The best "antiparallel" model a_1 was found to have similar energy to the $\bar{P}_1$ model and was statistically equivalent to the latter as regards the R'' factor. Projections of the P_1 and a_1 models onto the a^*c plane are illustrated in Figs. 7 and 8.

Despite the differences between the directions and polarities of the chains in the P_1, $\bar{P}_1$, and a_1 models, the chain conformations and the hydrogen bond systems are virtually similar in all three models. In each of the symmetrically independent layers, the chains are in a conformation close to *B*1 with the system of intramolecular hydrogen bonds O(3)H...O(5′) and O(2)H...O(6′) characteristic of *B*1. The macromolecules within the layer are linked via the intermolecular O(6)H...O(3″) hydrogen bonds, while the interlamellar hydrogen bonds are absent from the system.

An interesting feature of the $\bar{P}_1$ model is its ability to be converted into the next model ($\bar{P}_2$) as a result of the jump of the proton at the O(6) atom in the central chain, while the positions of all the remaining atoms remain virtually unchanged. The $\bar{P}_1 \rightarrow \bar{P}_2$ transition is accompanied by the rupture of the O(6)H...O(3″) intermolecular bond and the formation of the O(4″)...O(6)H...O(5″) interlamellar biacceptor bond. The similarity of the $\bar{P}_1$ and $\bar{P}_2$ models as regards structure and energy and also the small barrier to the transition make it possible to regard these two models as a single structural model with a labile system of hydrogen bonds.

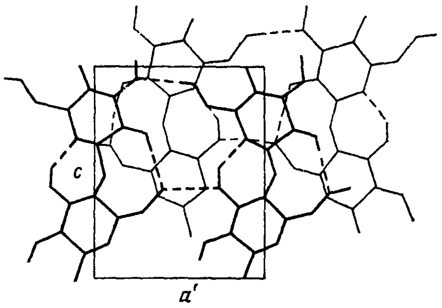

Figure 7. The $\bar{P}_1$ structural model corresponding to the global minimum in the target function Φ [Eqn.(7)] within the framework of the parallel version of the packing of the chains.[95,96]

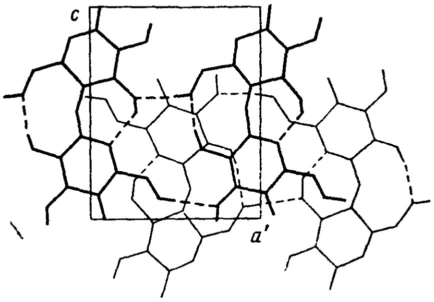

Figure 8. The a_1 structural model for CI corresponding to the global minimum in the target function Φ [Eqn.(7)] within the framework of the antiparallel version of the packing of the chains.[95,96]

A small energy barrier (<1 kcal mol^{-1}) is observed also for the $a_1 \rightarrow a_3$ and $a_1 \rightarrow a_4$ transitions. However, in these cases the probability of the transition is very insignificant owing to the large differences in the relative shift of the layers (~0.7 Å) between the models indicated. Clearly, such a shift requires the concerted collective displacement of the atoms within the limits of the target layer, which is an extremely improbable event. (Formally this implies that the pre-exponential factor in the expressions for the probabilities of the $a_1 \rightarrow a_4$ transitions is very small).

2. Cellulose II

The CII structural modification is formed when cellulose is regenerated from its derivatives or on reprecipitation from solutions [regenerated cellulose (RC)] and also when cellulose preparations are treated with concentrated solutions of alkali metal hydroxides [mercerised cellulose (MC)].[9-11] The regenerated and mercerised celluloses are characterised by virtually identical X-ray diffraction patterns and IR spectra and on this basis they are regarded as a single polymorphic modification.

Whereas well-resolved X-ray diffraction patterns typical of CII can be obtained on mercerising cotton, ramie, and wood cellulose, the attempts to obtain CII by mercerising the *Valonia ventricosa* fibres were not successful.[28,89,94] This confirms yet again the above hypothesis that cellulose from seaweed apparently possesses an individual crystal structure different from that of ramie, cotton, and wood cellulose.

It is important to note that the polymorphic transition from CI to CII is monotropic. The claim that CII is the more stable polymorphic modification of cellulose is based on precisely this experimental fact.

Analysis of the equatorial reflections in the X-ray diffraction patterns of CII shows that the CII unit cell is analogous to that in CI. One macromolecule intersects the *ab* face at the beginning of the crystallographic coordinate system, while the other makes an intersection of the centre of the face. It follows from the analysis of the intensities of the (110) and (020) reflections that the average plane of the glucopyranose rings in CII should be rotated by a somewhat greater angle relative to the *ac* plane than in CI.

The polymorphic transition from CI to CII is accompanied by significant changes in the IR spectra. Thus, whereas three bands with parallel dichroism (at 3275, 3350, and 3375 cm^{-1}) and two bands with perpendicular dichroism (at 3305 and 3405 cm^{-1}) are observed in the CI spectrum in the region corresponding to the vibrations of the OH groups, in the CII spectrum two bands with parallel dichroism (at 3407 and 3488 cm^{-1}) and three bands with perpendicular dichroism (at 3175, 3305, and 3350 cm^{-1}) are observed.[9,90] The above differences (both in the stretching vibration frequency of the OH groups and in the dichroism) indicate a significant rearrangement of the hydrogen bond system on passing from CI to CII. X-Ray diffraction patterns of CII were first obtained and indexed by Andress[99] within the framework of a monoclinic unit cell for the $P2_1$ space group. The unit cell parameters were a = 8.14 Å, b = 9.19 Å, c = 10.3 Å (fibre axis), and γ = 118°. Thus CII has lattice periods similar to those in CI but a significantly different monoclinic angle γ.

Crystallographic studies on CII were carried out simultaneously with such studies on CI using the same method and frequently the same workers were involved.[72,84,87,89,100,101] This obviates the need for .... structural CII models with parallel and antiparallel .... the CII models proper.†

As for CI, it is best to begin a detailed examination of structural models with the model put forward by Jones,[58,59] who examined structural CII models with parallel and antiparallel packing of the chains. A satisfactory agreement with IR spectroscopic and X-ray diffraction data was achieved for the model with the opposite direction of the chains and the shift S = 0.29. The positions of the O(6) atom in the angular and central chains were close to the *tg*-conformation

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†Parts of the Russian text appear to be missing (Translator).

and *gt*-conformation respectively. The angular chain was stabilised by the two intramolecular hydrogen bonds O(3)H...O(5′) and O(2)...O(6′) and the single central bond O(3)H...O(5′). The intermolecular bonds were in the (110) plane. These are two symmetrically non-equivalent hydrogen bonds of the O(6)...O(3″) type and the O(2)...O(2″) bond.

In the analysis of the structure of CII, Kolpak and Blackwell[63,102] used the approach proposed by Gardner and Blackwell[64] for the elucidation of the structure of CI. The same four trial models P_1, P_2, a_1, and a_2 were used as the initial approximation as in the analysis of the packing of CI. Both regenerated and mercerised celluloses were examined.

The optimised a_2 model, which is also free from short contacts, was found to be most suitable as regards the R'' factor. Application of Hamilton's test showed that, in terms of the R'' factor, the models obtained from a_1, P_1, and P_2 can be rejected for a level of significance higher than 99%. Comparison of the a_2 models optimised with respect to X-ray diffraction data for RC on the one hand, and MC, on the other showed that they are fairly similar but not identical. The main difference is in the value of the parameter S, which is 0.216 for RC and 0.227 for MC. Significant differences are observed also in the optimised values of the average isotropic temperature factor B_T, which are 20 Å^2 for RC and 32 Å^2 for MC.

The system of hydrogen bonds in the a_2 model resembles the system of such bonds in the Jones model.[59] The O(6)...O(3″) bond is located in the plane of the central chains, while the O(6)...O(2″) bond is in the plane of the angular chains. The O(2)...O(2″) bond is located in the (110) plane. According to the authors,[63,102] the presence of the last bond is in fact the main and fundamental difference between the structures of CI and CII and is the main cause of the increased stability of the CII polymorphic modification.

The structure of CII was also examined by Stipanovic and Sarko.[35] The optimum structural model of CII was selected from the condition for the minimum in the target function (5) with all the geometrical variables, including the bond lengths and the valence and torsional angles, varied. The average isotropic temperature multiplier was likewise varied. The model with the antiparallel disposition of the chains, which is close in terms of its parameters to the structural models of RC and MC proposed by Kolpak and co-workers,[63,102] was found to be most suitable. However, according to the author's calculations,[35] apart from the O(2)...O(2″) bond in the (110) plane there is also a possibility of the formation of the interlamellar O(6)...O(3″) bond.

A structural model of CII with a parallel arrangement of the chains has been proposed recently.[103] The unit cell in this model is made up of the diagonals of the Wellard cell and includes one symmetrically independent chain. This study[103] was based on the existing definite similarities between the X-ray diffraction patterns and IR spectra of CII and cellotetraose, whose unit cell contains one crystallographically non-equivalent molecule.[104] However, the above model[103] had an inadmissibly high value of the R factor ($R = 0.50$) and in addition conflicted with data for the IR dichroism of the stretching vibrations of the OH groups. This attempt demonstrates perhaps the error of the "mechanical" transfer of data obtained solely on the basis of a single model compound (cellotetraose) to the structure of a complex polymer such as cellulose.

The energy criteria have been resorted to in order to determine the structure of CII.[98,105,106] The optimum structural model was sought in a manner fully analogous to the method described above in the discussion of the studies by Nugmanov and co-workers.[61,95,96] The characteristics of the most probable structural models of CII are presented in Table 2. The following factors are striking in the analysis of Table 2. Firstly, it is evident that in the case of CI the available diffraction data are too few for an unambiguous solution of the structural problem (for a 99% level of significance, all the models presented are statistically equivalent). Secondly, comparison of the data in Tables 1 and 2 shows that the optimum models of CII are more favourable on energy grounds than the optimum models of CI by approximately 1–2 kcal mol^{-1}, which agrees with the view that CII is a more stable polymorphic modification of cellulose. Finally, it is seen from Table 2 that, among the models most suitable as regards energy, there are no models with a parallel arrangement of the chains. The difference of approximately 2 kcal mol^{-1} obtained between the best parallel model (P_1) and the best antiparallel models is sufficiently convincing to reject the hypothesis of a parallel arrangement of the chains in CII.[103] Among the antiparallel models in Table 2, mention should be made of the a_6 model, which is in essence a structural analogue of the familiar model of Stipanovic and Sarko[35] and also of Kolpak and co-workers.[63,102] Evidently the a_6 model is appreciably inferior to the best antiparallel models as regards energy and the value of the target function.

Table 2. Certain characteristics of the most probable structural models of CII.[98,105,106]

Model*	R''	U, kcal mol^{-1}	Φ, cal mol^{-1}	Model*	R''	U, kcal mol^{-1}	Φ, cal mol^{-1}
a_1	0.179	—21.4	—18.7	a_5	0.186	—20.4	—17.6
a_2	0.178	—21.2	—18.5	a_6	0.124	—19.4	—17.5
a_3	0.183	—21.2	—18.5	P_1	0.167	—19.4	—16.9
a_4	0.164	—20.1	—17.6	P_1	0.164	—17.5	—15.1

*The same notation is used as in Table 1.

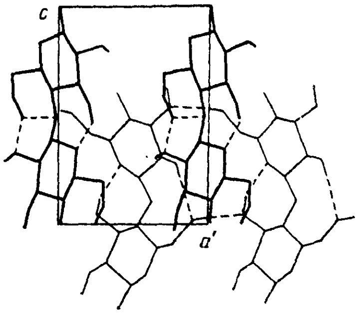
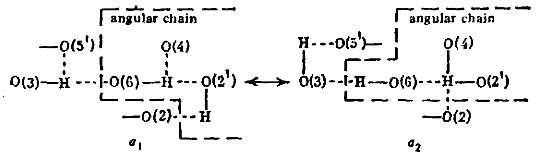


Figure 9. The optimum structural model a_1 for CII.[98,105,106]

The a_1 model, whose projection on to the $a'c$ plane is illustrated in Fig.9, is best in terms of the value of the target function. Evidently the a_1 model represents alternating layers parallel to the ac plane. The (020) layer in the a_1 model is constructed analogously to the layers in the structural a_1 and P_1 models for CI described above in the discussion of the studies of Nugmanov and co-workers.[95,96] In the (020) layer there are the intramolecular hydrogen bonds O(3)...O(5′) and O(2)H...O(6′) and the intermolecular bond

O(6)H...O(3″). The conformation of the macromolecules in the (010) layer of angular chains is close to the *A*1 conformation with its typical O(4)...O(6)H...O(2) biacceptor bond. There are no intermolecular hydrogen bonds in the (010) plane. The neighbouring layers in the a_1 model are linked by intermolecular bonds: the strong O(2)H...O(2″) bond and the weak O(3)H...O(6″) bond. The proton at O(3) is then found to be involved in the O(5′)...O(3)H...O(6″) biacceptor bond.

The a_2 structural model can be obtained from a_1 by changing the orientation of the O(6)H and O(2)H hydroxyls of the angular chain and the a_3 model can be obtained by altering the orientation of the O(6)H hydroxyl in the central chain. The rearrangement of the hydrogen bond system in the transition from the a_1 model to the a_2 model is illustrated schematically below (for clarity, only the hydroxyls involved in the rearrangement are shown); the OH groups of the angular chain are differentiated by a dashed line):



The hydrogen bond system remains uninvolved in the $a_1 \rightarrow a_3$ transition and only the position of the proton at the O(6) atom changes relative to the line connecting the donor and acceptor oxygen atoms.

It is seen from Table 2 that the a_1, a_2, and a_3 structures have similar energies and in addition the barriers to the transitions between them are low (0.9 and 0.2 kcal mol^{-1} for the $a_1 \rightarrow a_2$ and $a_1 \rightarrow a_3$ transitions respectively). As for the $\overline{P}_1$ and $\overline{P}_2$ models of CI, this factor suggests that all three structures can exist simultaneously in CII and can be interconverted as a result of the thermal migration of protons.

IV. CONCLUSION

Analysis of the data presented shows that the problem of the determination of the molecular-crystal structure of cellulose is still far from its final solution. In fact only the data for the symmetry and size of the unit cell as well as the conformation of the glucopyranose residue in the main macromolecular chain can now be regarded as fully non-controversial information about the structure of cellulose. The data enumerated do not, however, allow the complete reproduction of the architecture of the crystal owing to the extensive conformational possibilities associated with the side groups and the wide variety of different versions of the disposition of the cellulose chains in the crystal arising from this. The available diffraction data are too limited to make an unambiguous choice between several alternative versions of the structure.

The semiempirical energy calculations, which apparently possess a greater "resolving capacity" than crystallographic criteria such as the *R* factor and the principle of close packing, can apparently help significantly in solving the structural problem. However, even in this case calculation yields several possible versions of the structure which have extremely similar energies.

In our view, a more well defined situation obtains for the stable CII polymorphic modification of cellulose where the most suitable model is separated from the remaining possible versions of the structure by an "energy gap" of approximately 1 kcal mol^{-1}. Bearing in mind that the error in the calculation of the lattice energy by the method of atom–atom potentials is usually systematic and is to a large extent compensated when different versions of packing of the same molecules are compared, one may expect that the ~1 kcal mol^{-1} energy difference is entirely significant. An interesting feature of the most probable model of CII is the lability of its hydrogen bond system, i.e. the capacity for ready rearrangements as a result of the thermal movement of individual protons.

In the case of CI the best models are distributed more or less uniformly with respect to energy and the best parallel and the best antiparallel models ($\overline{P}_1$ and a_1 in Table 1) are almost equivalent as regards energy and are statistically indistinguishable with respect to the R'' factor. An important argument in support of the antiparallel version of the structure is the finding that the fibres swell only slightly on mercerisation leading to the transition of CI into CII. An appreciable structural rearrangement (in particular in the change of the arrangement of the chains) cannot then occur, which entails a different similarity of the structures of CI and CII. Comparison of the a_1 models for CI and CII does indeed reveal a similarity of significant parameters such as the orientation of the hydroxymethyl groups and the relative shift of the chains.

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The Synthesis and Polymerisation of Macromonomers

K.S.Kazanskii, P.Kubisa, and S.Penczek

Problems concerning the synthesis and reactions of macromolecular monomers (macromonomers)-polymeric molecules containing at least one polymerisable, usually unsaturated, end group or a fragment capable of polycondensation reactions—are considered. They are usually obtained by a radical or ionic polymerisation method in which the use of special chain initiating or terminating agents as well as intense chain transfer ensures the introduction of the reactive group. Studies on the polymerisation and copolymerisation of macromonomers are surveyed and the characteristic features of these processes, determined by the low concentration of the reacting group and the presence of a polymeric substituent, are analysed. The applications of macromonomers in polymer engineering, mainly in the synthesis of cone, star, graft, and other hybrid polymers, are examined.

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I. INTRODUCTION

Reactive oligomers constitute a large family of polymers having at least one functional end group capable of further reactions. Macromolecular monomers or macromonomers (MM) are reactive monofunctional oligomers capable of participating in chain propagation reactions via these groups. The term macromonomer (or even more briefly "macromer") was introduced by Milkovich[1] as the trade name for a group of polystyrene oligomers with a wide variety of polymerisable end groups. According to a later definition,[2] macromers are short-chain polymers coupled quantitatively at one of the ends of the chain to polymerisable unsaturated groups. The unsaturation is naturally not the only possible source of the polymerisability of MM, since the end group can be cyclic or of another type, although the number of examples of such groups is small. These groups can be introduced into the MM molecule in the stage involving the initiation or limitation of the growth of the chain (chain transfer and termination) and also as a result of the conversion of one set of end groups into another.

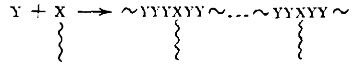
In reality MM were known long before the time when this term appeared. Thus siloxane MM with styrene groups (polysiloxanestyrene MM) were synthesised as early as 1962 and were used to obtain polystyrene with grafted polysiloxane side chains.[3] All these features resemble the history of "living" polymers, which existed long before they came to be referred to by this term, but the introduction of the latter was extremely useful for the purposes of classification and the elucidation of preparative possibilities.

Thus a MM can be represented schematically as a polymer chain having one end group X capable of entering into chain propagation reactions:

$$\sim\!\sim\!\sim X$$

although in a number of studies bifunctional and even polyfunctional oligomers of different type have also been classified as MM, which is incorrect.

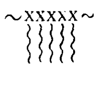
When preparative aspects associated with MM are considered, then MM are usually regarded as intermediates in the synthesis of graft copolymers with a vigorously defined structure, in particular as regards the length of the grafted chains:



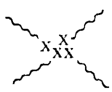
$$Y + \underset{\wr}{X} \longrightarrow \sim YYY\underset{\wr}{X}YY\sim \ldots \sim YY\underset{\wr}{X}YY\sim \qquad (1)$$

where Y is a low-molecule-weight comonomer.

The homopolymerisation of the MM itself affords a regular comb polymer (I), while in the case of very low degrees of polymerisation the same reaction leads actually to a star polymer (II):



(I)



(II)

Together with other familiar methods of preparative polymer chemistry, the procedures based on MM give rise to the prospect of obtaining polymeric products of the types indicated, whose nature is extremely varied. The possibility of combining in a single macromolecule units of the kind that cannot be joined together by direct or successive copolymerisation and other similar methods is of special interest. Thus macromonomers give rise to the possibility of overcoming the inability of certain monomers to polymerise via a single mechanism.

MM are identified by the usual methods, characterising mainly the molecular weight ($\overline{M}_n$) and the average functionality ($\bar{f}_n$) with respect to the groups X:

$$\bar{f}_n = \frac{\overline{M}_n N_x}{g},$$

where g is the mass of the sample analysed and N_x the number of functional groups found in the specimen. It is noteworthy that, in contrast to the telechelic polymers used in the synthesis of polymer networks, in the case of MM there is no need to attain a high functionality, although naturally in most synthetic studies the authors endeavoured to obtain compounds with a functionality close to unity. The deficiency of polyfunctional reactive oligomers as regards functionality usually has serious consequences when they are employed in the synthesis of polymeric materials.[4]

II. METHODS OF SYNTHESIS OF MACROMONOMERS

Polymerisable groups can be introduced into the macromolecule in virtually any stage of its formation process. In polymerisation such groups can be a direct result of a specific mechanism of chain initiation, destruction, or transfer and also of the introduction into the reactive mixture of special substances (chain initiating, terminating, or transferring agents). Finally, groups capable of subsequent polymerisation can be formed during the reaction of some other end groups which were present in the initial oligomers and in this case polycondensation oligomers can also be employed for the synthesis of MM.

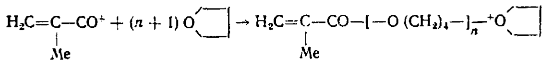
1. Polymerisation Methods

(a) Initiation

Initiation with subsequent "living" polymerisation is one of the most direct methods of synthesis of MM. It is necessary that the initiation under the influence of the initiator introduced should be the only reaction leading to the appearance of growing polymer chains and that side processes, including the polymerisation of the end group formed, should not occur. We shall consider certain examples of such syntheses.

Cationic polymerisation. Only a few monomers polymerise via the "living" mechanism under the conditions of cationic initiation. Some of them are used to synthesise MM.

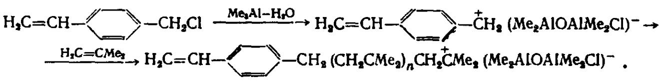
The polymerisation of tetrahydrofuran under the influence of the unsaturated acylium salt (III), i.e.



(III)

leads to a polymer the first of the end groups of which is the methacrylate group, while the second is available for the generation of any kind of functional group.[5] This method is suitable for the "living" cationic polymerisation of various monomers, because the oxocarbenium ions (III) can initiate the polymerisation of heterocycles such as acetals, sulphides, and amines.

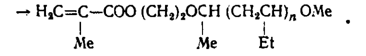
A study,[6] whose authors were the first to synthesise polyisobutylene MM using as the initiator the p-vinylbenzyl chloride—Me_3Al—water system under conditions ruling out chain transfer, may serve as an example of the employment of the cationic polymerisation of vinyl monomers:



The number of styryl groups per chain in the MM synthesised was close to 1.0 according to UV spectrophotometric data (255 nm, $\varepsilon = 1.68 \times 10^4$ litre mol^{-1} cm^{-1}), but the authors[6] noted some decrease of functionality with respect to these groups when the synthesis was carried out at low monomer concentrations or with high degrees of conversion. In a modified method,[7] the initiator employed was therefore p-(β-bromoethyl)cumenyl chloride, which, after its incorporation in the chain, was converted into the styryl group by treatment with potassium t-butoxide.

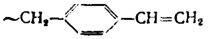
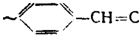
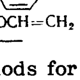
Certain characteristics of the MM based on isobutylene obtained by these procedures are presented in Table 1, which also includes information about isobutylene MM synthesised by other methods.

The polymerisation of vinyl ethers on treatment with the $HI-I_2$ system takes place without chain termination and transfer and leads to monodisperse polymers. This fact was used to synthesise MM from ethyl vinyl ether:[11]



$$H_2C{=}\underset{Me}{C}{-}COO(CH_2)_2OCH{=}CH_2 + nEtOCH{=}CH_2 \xrightarrow{HI-I_2} H_2C{=}\underset{Me}{C}{-}COO(CH_2)_2O\underset{Me}{CH}(CH_2\underset{Et}{CH})_nOMe\ .$$

Table 1. Characteristics of MM based on polyisobutylene.

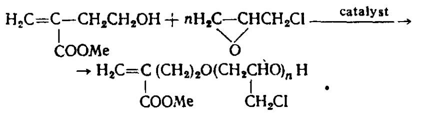
End group	Method*	$10^{-3}\bar{M}$	$\bar{f}_n$	Refs.
	A	10—30	—	[6]
	A	4.2—34.2	0.9—1.1	[7]
$\sim CH_2{-}\underset{Me}{C}{=}CH_2$	B	1.6—3.2	0.95—1.04	[8]
$\sim CH_2OCO\underset{Me}{C}{=}CH_2$	B	1.6—13.9	0.98—1.05	[8]
	C	27.0	1.0	[9]
$\sim CH_2OCOCH{=}CH_2$	B	3.6	1.95**	[10]

*Methods for the introduction of end groups: A–initiation; B–reactions via end groups; C–method employing a combined agent–initiator and chain transfer agent ("inifer"[9]).

**A bifunctional derivative.

The polymerisation was carried out at −40 °C in toluene; chain termination was achieved by introducing methanol. The degree of polymerisation was varied by varying the ratio of the monomer and the initiator in the range 5–100. A study of the MM obtained by gel-permeation chromatographic (GPC) and NMR methods confirmed the proposed structure.

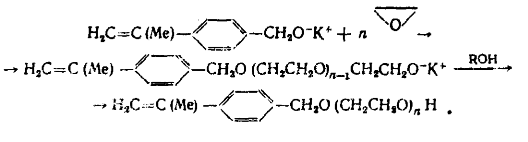
Recently, in the development of methods for the preparation of oligomers having a specified structure on cationic initiation, much hope was associated with the so called "activated monomer" mechanism, which makes it possible to avoid many typical complications, in particular macrocyclisation. This procedure, in which a proton-containing initiator "specifies" the polymer end group, has been used recently to obtain MM based on epichlorohydrin:[12]



It is entirely possible that this approach is fairly universal.

Anionic polymerisation. The range of monomers polymerising via the "living" mechanism under the conditions of anionic initiation is much wider than in the cationic processes. Anionic polymerisation reactions of styrene and its derivatives, dienes (buta-1,3-diene, isoprene), 2- and 4-vinylpyridines, methacrylates (under conditions ruling out chain transfer), certain cyclic ethers (usually epoxyethane), three- and four-membered cyclic sulphides, lactones, cyclosiloxanes,[†] and other less readily available groups of monomers can be used virtually without limitations for the synthesis of MM by the direct initiation procedure. The formation of living polymers is not the only precondition for the successful synthesis of MM: it is necessary that the initiation mechanism should ensure the incorporation of the future polymerisable group in the polymer chain.

For example, alkoxides derived from p-isopropenylbenzyl alcohol have been used to synthesise polyoxyethylene MM:[13]

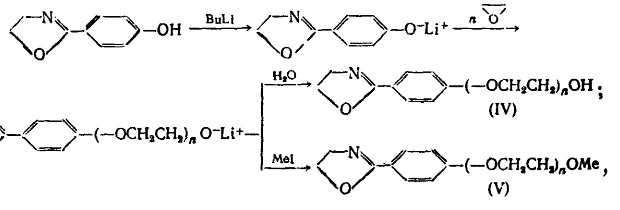

(2)

The MM, formed in 75–85% yield, had molecular weights in the range 2000–4500. They were characterised by different methods; it has been shown that the calculated and observed characteristics agree satisfactorily. The molecular weights of two specimens based on the data of Masson et al.[13] are presented below:

From the ratio of the monomer and initiator concentrations	2000	4500
From the titration of unsaturated groups	1850	5200
From ^{1}H NMR data—the ratio of the signals of the protons in the aromatic end groups and oxyethylene units	1700	4700
From the UV spectrum (250 nm, ϵ = 12 700 litre mol^{-1} cm^{-1})	2000	4200
From light scattering data	2100	4500

The results of the study of Masson et al[13] show that the process does indeed proceed via mechanism (2), but a high functionality is hardly guaranteed in this instance, because any proton-containing admixture participates in this process as a coinitiator (see, for example, Sepulchre et al.[14]), generating chains without specified functional groups.

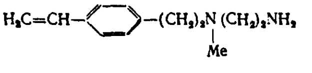
Polyoxyethylene MM with 2-oxazoline end groups, suitable for subsequent cationic polymerisation, were synthesised in an analogous way.[15] When the reactions are carried out in accordance with the scheme

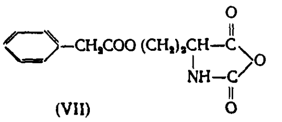


the MM (IV) and (V) are obtained, their degrees of polymerisation amounting to ~20 and 40 respectively according to gas-phase osometric data; a chain length of ~20 can also be obtained from the ratio of the peak areas of the methylene and aromatic protons in the NMR spectrum of compound (IV); compounds (IV) and (V) homopolymerise and copolymerise on treatment with BF_3 etherate.

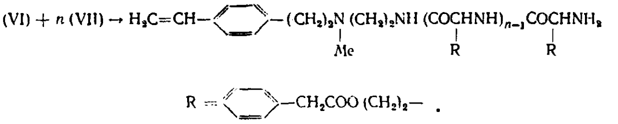
Here mention should also be made of the synthesis of reactive oligomers of epoxyethane and propene on treatment with alkoxides derived from allyl alcohol,[16] but in this case there is even less guarantee of the formation of MM homogeneous as regards functionality since intense chain transfer to the monomer is characteristic of the polymerisation of epoxypropane.

It is known that the polymerisation of the *N*-carboxyanhydrides of α-aminoacids on treatment with primary amines proceeds in many instances with quantitative initiation via addition to the monomer. This has been used[17] for the synthesis of polyaminoacid MM, which are of great interest from the standpoint of their subsequent use for the preparation of biomedical materials. Amino-derivatives of styrene, for example compound (VI), were used as the initiators, while the monomer was the *N*-carboxyanhydride of γ-benzyl-L-glutamic acid (VII):

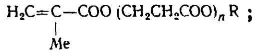

(VI)


(VII)

The polymerisation reaction via mechanism (3) leads to MM with a styrene end group:


(3)

Salts of various weak acids, which are effective only in the presence of activators such as crown ethers, are known to be suitable for the initiation of the polymerisation of β-propiolactone. The use for this purpose of the potassium methacrylate–dibenzo-18-crown-6 ether made it possible to obtain the corresponding MM:[18]



$$\underset{\text{Me}}{\underset{|}{H_2C{=}C}}{-}COO\,(CH_2CH_2COO)_n\,R\ ;$$

R = H, CH_2Ph .

with a molecular weight of 1000–15 000 and with a quantitative functionality. An analogous approach is applicable also to epoxyethane.

b) Reactions Involving the Deactivation or Destruction of Active Centres

Cationic polymerisation. "Living" cationic polymerisation mechanisms, which constitute an essential condition for the quantitative introduction of the required end groups at the deactivation stage, has been established most reliably for heterocycles. It has been correctly stated recently,[19] in the analysis of the problem of the introduction of functional end groups under the conditions of cationic polymerisation with ring opening, that the main obstacle in this instance is chain transfer to the polymer, which should be eliminated or negligible. Macrocyclisation gives rise to analogous difficulties.

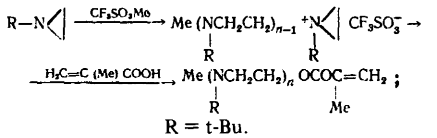
There are virtually no complications in the preparation of MM from tetrahydrofuran, cyclic sulphides, or aziridines if the process is carried out up to low degrees of conversion. At later stages of the process, chain transfer to the polymer complicates the synthesis of MM in these and similar systems and the problem is not limited to macrocyclisation, the broadening of the molecular weight distribution (MWD), and the impossibility of achieving total conversion. An even more serious obstacle is the disproportionation of living polymers, in which they are partly converted into a mixture of inactive and bifunctional growing macromolecules:

$$AAA^* + AAA^* \rightarrow AA + {}^*AAAA^*$$

which completely rules out the possibility of obtaining MM homogeneous as regards functionality during their subsequent deactivation.

[†] Macrocyclisation at high degrees of conversion is characteristic of the last two groups of monomers.

The use of sterically hindered monomers partly or fully suppresses the undesirable chain transfer to the polymer; one of the examples of this is provided by the successful synthesis of methacrylate MM from *N*-t-butylaziridine:[20]

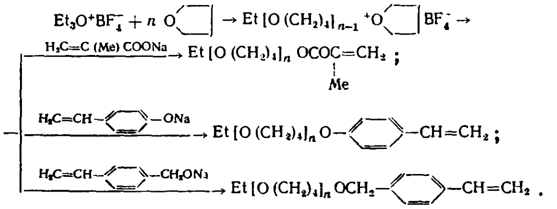


R = t-Bu.

Gas-phase osmometric and ^{1}H NMR data confirm the structure of the MM obtained, whose finite functionality was not determined in the above study.

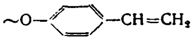
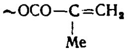
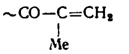
Many different MM have been obtained from tetrahydrofuran, which is perhaps the most typical monomer polymerising via the cationic "living" mechanism.

MM have been synthesised[21-23] from tetrahydrofuran with methacrylate and styrene end groups via mechanism (4), the polymerisation being interrupted by introducing the appropriate reagents at a low degree of conversion:



(4)

Table 2. Characteristics of MM based on polytetrahydrofuran obtained by cationic polymerisation methods.

End group	Method*	$10^{-3}\bar{M}$	$\bar{f}_n$	Refs.
	A	2.7—9.7	0.93—1.07	[21]
	A	2.3—8.0	—	[24]
	A	4.5—9.9	0.90—1.12	[23]
 $\sim OCO{-}C(Me){=}CH_2$	A	8.0	0.98—1.00	[22]
 $\sim CO{-}C(Me){=}CH_2$	B	1.6—3.4	0.93—1.08	[5]
$H_2C{=}C(R){-}CO{\sim}OCO{-}C(R){=}CH_2$	C	17.0—55.4	1.71—1.96**	[25]

*Methods for the introduction of end groups: A—deactivation; B—initiation; C—the method of "inifers" (see the footnote to Table 1).

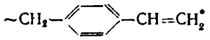
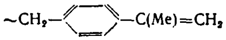
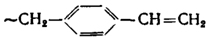
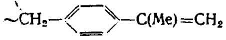
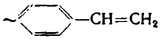
**Bifunctional derivative (R—H or Me).

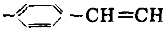
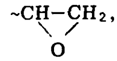
Other functional groups have been introduced into polymers via procedures similar to scheme (4). Certain characteristics of MM based on tetrahydrofuran, obtained by the deactivation of living polymers and also by other ionic polymerisation methods, are listed in Table 2. Evidently in most cases, where the reaction is continued only up to a low degree of conversion, the target functionality is nearly obtained. There is no doubt that a wider assortment of polymerisable end groups is also possible.

Anionic polymerisation. The synthesis of MM by the method involving the directed deactivation of living anionic polymers was achieved for the first time in relation to polystyrene.[1,26,27] A multiplicity of different functional groups, capable of polymerisation via a multiple bond or with ring opening and also of polycondensation or polyaddition, were introduced.

The deactivation of macroanions leads to much more extensive possibilities than in the case of the analogous cations, because, as already mentioned, a much greater number of monomers polymerise in this instance with formation of living polymers. The realisation of these possibilities is illustrated in Table 3, where the majority of the MM obtained by this procedure at the present time are listed. The method for the introduction of functional groups in the synthesis of all the MM investigated is in principle the same and consists in the reaction of the nucleophilic living macroanion (usually in the state of an ion pair) with an electrophilic deactivator.#

Table 3. Characteristics of MM obtained by the deactivation of "living" anionic polymers.

Polymer chain	Polymerisable group	$10^{-3}\bar{M}$	$\bar{f}_n$	Refs.
Polystyrene		3.8—6.0	0.95—1.10	[28]
Polyoxyethylene	$\sim OCO{-}C(Me){=}CH_2$	2.0—4.5	0.87—1.10	[13]
Poly(methyl methacrylate)		1.9—7.0	0.87—1.06	[29,30]
,,	$\sim CH_2CH{=}CH_2$	1.3—1.4	—	[29,30]
Polyamide**		3.7—3.8	0.93—1.07	[31]
Polyvinylpyridine	$\sim(CH_2)_2OCO{-}C(Me){=}CH_2$	3.5—6.2	0.70—0.94	[32]
,,		1.1—4.3	0.70—0.93	[32]
Polydimethylsiloxane		3.1—7.4	0.90—1.02	[33]
,,	$\sim(CH_2)_5OCOC(Me){=}CH_2$	3.2—7.7	0.92—1.05	[33]

*MM based on polystyrene with the groups $\sim CH{=}CH_2$, $\sim C(Me){=}CH_2$, $\sim OCH{=}CH_2$, , , $\sim OCOC(Me){=}CH_2$, $\sim OCOCH{=}CH{-}COOH$, $\sim CH_2COOCH{=}CH_2$, and $\sim CH(OH){=}CH_2OH$ have been obtained,[1,26,27] but have not been characterised quantitatively.

**Polymer of 8-oxa-6-azabicyclo[3.2.1]octan-7-one.

The probability of side reactions, i.e. the non-selectivity of the reaction involving the introduction of the functional group, increases with increasing reactivity of the anion. Its conversion into a less active form yields in many instances positive results, of the kind achieved, for example, by the preliminary conversion of the polyvinylpyridine carbanion into an oxa-anion by reaction with epoxyethane.[32]

#The polymerisation of a bicyclic oxalactam, which proceeds via the activated monomer mechanism, is an exception;[31] in this instance the anion of the deactivator attacks the growing end of the chain.

Radical polymerisation. One of the possible mechanisms of chain termination in radical polymerisation is disproportionation of the macroradicals in accordance with the scheme

$$2\sim CH_2\dot{C}HX \rightarrow \sim CH{=}CHX + \sim CH_2CH_2X \ .$$

This reaction leads to a polymeric product, half of the macromolecules of which contain an unsaturated end group. This termination mechanism predominates in the polymerisation of methyl acrylate, methyl methacrylate, and other monomers.[34] We may note that, owing to the higher activation energy than in the recombination reaction, the contribution of the disproportionation to the destruction of macroradicals increases with increasing temperature. However, the tendency towards the formation of symmetrically substituted double bonds does not give rise to prospects for the use of such MM owing to their low reactivity.

(c) Chain Transfer

The synthetic applications of the chain transfer reaction as a method for the introduction of functional groups require that it should proceed effectively, predominating among other reactions limiting the length of the polymer chain. It is desirable that the chain transfer agent should not influence the polymerisation kinetics, i.e. that the new species arising in the chain transfer step should initiate the next chain. In essence, this is merely the definition of true chain transfer. Chain transfer systems and agents acting according to this principle have long been known, especially in radical polymerisation.

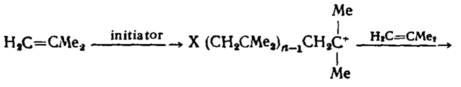
There are several radical and ionic polymerisation processes in which MM are formed via a mechanism natural for these processes, i.e. without the introduction of any special chain transfer agents. The most obvious variant of this method of synthesis of MM is polymerisation with intense chain transfer to the monomer. Generally speaking, two cases are possible, for example, for vinyl monomers:

$$\sim CH_2\dot{C}HX + H_2C{=}CHX - \begin{cases} \xrightarrow{a} \sim CH_2CH_2X + H_2C{=}\dot{C}X \ ; \\ \xrightarrow{b} \sim CH{=}CHX + Me\dot{C}HX \ . \end{cases} \qquad (5)$$

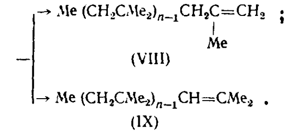
If there are no other initiation and termination processes in the given system, the double bond is fixed in the initial (pathway *a*) or terminal (pathway *b*) fragment of the chain. Chain transfer of type (5) in processes of different chemical nature proceeds with transfer of a hydrogen atom, proton, hydride ion or, more rarely, a larger species.

Cationic polymerisation. Two types of chain transfer reactions lead to MM in cationic polymerisation—chain transfer to the monomer and elimination of a proton from the active fragment of the growing macromolecule.

Chain transfer to the monomer is characteristic of the cationic polymerisation of certain unsaturated compounds. It has long been known, for example, that the cationic polymerisation of isobutene results in the formation of a macromolecule containing unsaturated groups at the end of the chain.[35,36] A more detailed analysis demonstrated that the number of such groups in the polymer is equal to the total number of macromolecules to within 5% (in the range of molecular weights 700–2000),[37] i.e. intense chain transfer takes place via the mechanism:



$$H_2C{=}CMe_2 \xrightarrow{\text{initiator}} X\,(CH_2CMe_2)_{n-1}CH_2\overset{\overset{\displaystyle Me}{|}}{\underset{\underset{\displaystyle Me}{|}}{C^+}} \xrightarrow{H_2C=CMe_2} \qquad (6)$$



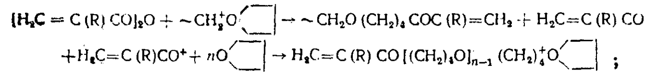
$$- \begin{cases} \rightarrow Me\,(CH_2CMe_2)_{n-1}CH_2\underset{\underset{\displaystyle Me}{|}}{C}{=}CH_2 \ ; \\ \qquad (VIII) \\ \rightarrow Me\,(CH_2CMe_2)_{n-1}CH{=}CMe_2 \ . \\ \qquad (IX) \end{cases}$$

NMR data have shown[37] that, together with groups (VIII) and (IX), other isomeric structures are formed in the MM via a reaction involving mechanism (6) but the entire wide variety of the different kinds of terminal unsaturation reduces exclusively to groups of type (VIII) when di-t-butylpyridine is used in the reaction as a cationic trapping agent.[38]

The cationic polymerisation of styrene[39] and α-methylstyrene[40] also leads to polymers with unsaturated end groups. They are formed in high yields in the polymerisation of styrene by CF_3SO_3H in non-polar media.[41] It has been established[42] that the yield of double bonds in acenaphthylene polymers formed via the cationic mechanism is quantitative.[42]

Reactions involving chain transfer to the monomer with formation of polymers having unsaturated end groups proceeds also in the polymerisation of certain heterocycles—ε-caprolactone,[43] oxepan,[44] and 2,2-dimethyloxetan.[45]

Transfer to the chain transfer agent, specially introduced into the system, has been used to obtain bifunctional MM. It has long been established[46] that acid anhydrides, for example, acetic anhydride, act as effective chain transfer agents in the polymerisation of tetrahydrofuran, which makes it possible to regulate the chain length and the composition of the end groups. This same procedure has been used recently to obtain bifunctional acrylate and methacrylate MM:[25,47]



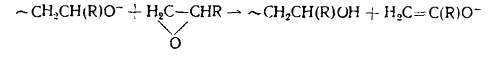
(7)

R = H, Me .

There is a purely formal analogy between reaction (7) and polymerisation under the influence of "inifers"—substances which act simultaneously as initiators and chain transfer agents and introduced into polymer practice by Kennedy.[48] In the studies already quoted[8–10] this method has been used to synthesise various polyisobutylene MM (see Table 1).

The use of effective proton trapping agents—the so called "proton sponges", especially di-t-butylpyridine which gives rise to effective proton transport—is also promising in this instance.

Anionic polymerisation. The best known instance of the direct formation of MM in ionic polymerisation is provided by processes involving substituted oxirans.[49] The increased acidity of the hydrogen atoms in the molecules of these monomers, on the one hand, and the presence of the highly nucleophilic alkoxide anions, on the other, increase sharply the rate of the processes involving chain transfer to the monomer:



(8)

whose contribution is extremely significant for the anionic polymerisation of the majority of substituted epoxides. We may recall that their oligomerisation processes are usually employed to generate hydroxylated telechelate polymers for the synthesis of polyurethanes and in this sense reaction (8) prevents the attainment of the required functionality.

These reactions have been studied in greatest detail in relation to epoxypropane, where two variants of terminal double bonds are possible:

$$H_2C{=}CH{-}CH_2O{\sim}\ \text{(X)} \qquad Me{-}CH{=}CH{-}O{\sim}\ \text{(XI)} \ .$$

Under the polymerisation conditions, the allyl groups (X) isomerise to the *cis*-propenyl groups (XI).[50] The maximum number of unsaturated groups does not, however, exceed 50–55% and their content depends on the temperature of the synthesis, the radius of the alkali metal counter-ion, which has been omitted in scheme (8), and also on the concentration of alcohol in the polymerisation system.[51,52] Reactions (8) have been observed also in the polymerisation of substituted glycidyl ethers: up to 87% of unsaturated macromolecules are formed in the polymerisation of, for example, *o*-chlorophenyl glycidyl ether and up to 79% in copolymerisation with epoxypropane.[52]

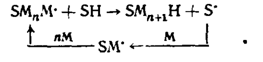
Since the introduction of polyether fragments into the macromolecules is of practical interest, the set of problems associated with chain transfer as a method of synthesis of MM requires a more serious analysis.

Chain transfer to the monomer is characteristic under certain conditions of the polymerisation of ethylene under the influence of Ziegler type catalysts,[53,54] which creates the possibility of the controlled conversion of ethylene into C_6–C_{20} α-olefins, which can then be used as MM. Mainly vinyl end groups are then formed and these then partially isomerise to internal double bonds. The fractions of vinyl groups β in ethylene oligomers are listed below:[54]

n	6	8	10	12	14	16	18
β, mole %	90.4	88.4	86.4	85.5	84.8	84.1	82.5

Variation of the monomer pressure, of the nature of the solvent, and other conditions makes it possible to increase the functionality with respect to these groups almost to 100%. The possibility of the quantitative epoxidation of α-olefins obtained by this method is of great interest,[55] because the subsequent copolymerisation of such MM opens a way to polyethers with hydrocarbon side chains.

Radical polymerisation. The formation of reactive oligomers (introduction of functional groups) with the aid of the chain transfer reaction has been the object of many investigations. The successful insertion of reactive groups into macromolecules via a chain transfer agent specially introduced into the system depends on the reactivity of the monomer (M) and the corresponding macroradical and also on the reactivity of the chain transfer agent (SH) in chain transfer and reinitiation processes:



$$SM_nM^{\cdot} + SH \rightarrow SM_{n+1}H + S^{\cdot};\quad S^{\cdot} \xrightarrow{M} SM^{\cdot} \xrightarrow{nM} SM_nM^{\cdot} \ . \qquad (9)$$

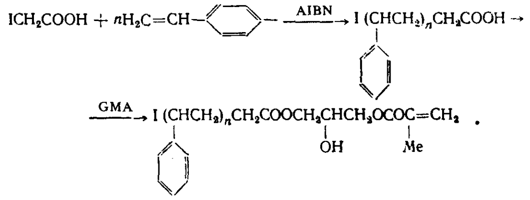
Thus the effectiveness of the reinitiation is low for inactive monomers, which give rise instead to reactive macroradicals, which are more reactive than the radical S in Scheme (9).

One of the most thoroughly investigated transfer processes having a practical application is the telomerisation of ethylene by CCl_4:[56]

$$CCl_4 + nH_2C{=}CH_2 \xrightarrow{R} CCl_3(C_2H_4)_nCl \ \text{(XII)} \ .$$

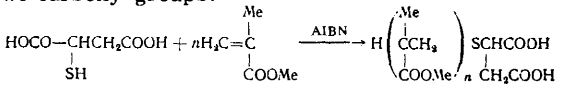
A wide variety of reactions of the telomer (XII) are possible and it can be regarded as the intermediate in the synthesis of MM. There are examples of the use of the telomerisation of various monomers for the direct synthesis of MM.[57–62]

The radical polymerisation of styrene and methyl methacrylate in the presence of iodoacetic or thioglycolic acids leads to a monocarboxylate polymer, into which functional groups have been introduced.[57,58] For example, styrene has been telomerised by treatment with azobisisobutyronitrile (AIBN) with subsequent introduction of functional groups by means of glycidyl methacrylate (GMA) in accordance with the scheme:



The reaction leads to the corresponding MM (with molecular weights of 4300–7700) in yields up to 90%.[58]

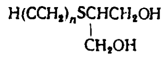
The use of thiomalic acid as the telogen makes it possible to introduce into the macromolecule a telechelic fragment with two carboxy-groups:[59]



$$HOCO{-}\underset{SH}{CH}CH_2COOH + nH_2C{=}\overset{Me}{\underset{COOMe}{C}} \xrightarrow{AIBN} H\left(\overset{Me}{\underset{COOMe}{C}}CH_2\right)_n\underset{CH_2COOH}{SCHCOOH} \ .$$

The authors[59] emphasise that this is the first synthesis of MM for subsequent polycondensation with diols, diamines, etc.

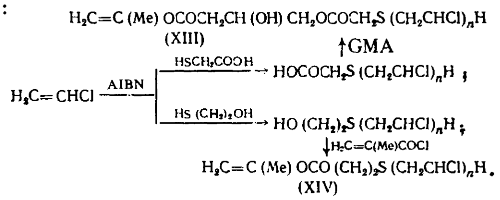
MM containing the diol group at one end of the poly(methyl methacrylate) chain have been obtained analogously using thioglycerol:[60]



$$H(CCH_2)_nS\underset{CH_2OH}{CH}CH_2OH \ ,$$

These MM can also be used in polycondensation or polyaddition reactions, for example, for the synthesis of modified polyurethanes.[60]

Radical telomerisation with subsequent introduction of unsaturated groups has been used recently to synthesise vinyl chloride and vinylidene chloride MM.[61,62] In the case of vinyl chloride, two different telogens were used and correspondingly two agents for the introduction of functional groups:



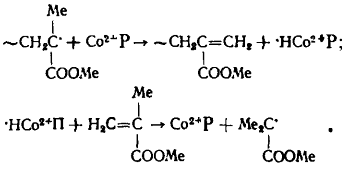
$$H_2C{=}CHCl \xrightarrow{AIBN}\ \xrightarrow{HSCH_2COOH} HOCOCH_2S(CH_2CHCl)_nH \xrightarrow{GMA} H_2C{=}C(Me)OCOCH_2CH(OH)CH_2OCOCH_2S(CH_2CHCl)_nH \ \text{(XIII)} \ ;$$

$$H_2C{=}CHCl \xrightarrow{AIBN}\ \xrightarrow{HS(CH_2)_2OH} HO(CH_2)_2S(CH_2CHCl)_nH \xrightarrow{H_2C=C(Me)COCl} H_2C{=}C(Me)OCO(CH_2)_2S(CH_2CHCl)_nH \ \text{(XIV)} \ .$$

The products (XIII) and (XIV) have been comprehensively characterised—they have molecular weights in the range 1000–2400 and copolymerise with standard monomers.

We shall now return to chain transfer to the monomer. By itself, this reaction is unable to ensure the required functionality under the usual conditions. In fact, for example, in the usual polymerisation of methyl methacrylate (in bulk at initial concentration 1 M, 50 °C, and rates of initiation in the range 10^{-8}–10^{-6} mol litre^{-1} s^{-1}), f_n with respect to unsaturated end groups does not exceed 0.3–0.4, which can be shown by estimates based on kinetic parameters.[34]

A sharp acceleration of chain transfer by catalysts has been observed and studied in detail recently.[63] It has been shown, for example, that in the presence of cobalt complexes of porphyrin $Co^{2+}P$, a hydrogen atom is transferred with a high efficiency from the radical to the monomer in the polymerisation of methyl methacrylate:



$${\sim}CH_2\overset{Me}{\underset{COOMe}{C^{\cdot}}} + Co^{2+}P \rightarrow {\sim}CH_2\underset{COOMe}{C}{=}CH_2 + {\cdot}HCo^{2+}P;$$

$${\cdot}HCo^{2+}\Pi + H_2C{=}\overset{Me}{\underset{COOMe}{C}} \rightarrow Co^{2+}P + Me_2\underset{COOMe}{C^{\cdot}} \ .$$

There are a number of pieces of evidence (obtained by NMR, electrochemical, etc. methods) for this mechanism, which results in the formation of a substituted methyl methacrylate group in each macromolecule.

(d) Other Polymerisation Methods

The polymerisation of acrylamide is initiated by lithium alkyls via a mechanism involving the abstraction of a proton with retention of the vinyl group:[64]

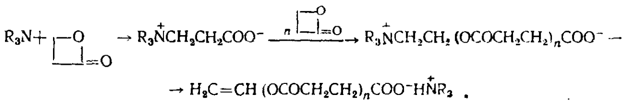
$$H_2C{=}CHCONH_2 + RLi \rightarrow RH + \underset{(XV)}{H_2C{=}CHCONH^-Li^+}\ .$$

The latter is then introduced into the chain of the poly-β-alanine (nylon-3) formed:

$$(XV) + nH_2C{=}CHCONH_2 \rightarrow H_2C{=}CHCONH\,(CH_2CH_2CONH)_n^-Li^+\ .$$

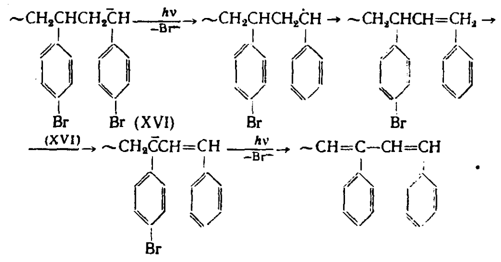
The highest functionality ($\bar{f}_n$ = 0.95–1.10) with respect to these groups has been shown to be attained[64] on initiation with t-butyl-lithium. The MM formed polymerises under the influence of radical and ionic initiators.[65]

The polymerisation of *N*-carboxyanhydrides on treatment with amines, which proceeds with retention of the initial group of the initiator at the end of the macromolecule, was examined previously. In the case of a number of monomers (for example, β-propiolactone, epoxyethane, etc.) and tertiary amines, the polymerisation is complicated by the instability of the primary zwitter-ionic active centres:



This instability leads to the appearance of unsaturated end groups in the macromolecules, which is analogous to the method of synthesis of olefins via the Hofmann rearrangement. In the polymers of β-propiolactone,[66] epoxethane,[67] and glycidyl phenyl ether,[68] there is a double bond in each macromolecule. It is essential to note that only the acrylate end groups of poly-β-propiolactone formed via this mechanism are of real interest from the standpoint of the possibility of the subsequent employment of MM.

A novel method for the generation of double bonds has been devised in a study of the photochemical decomposition of living poly-*p*-bromostyrene:[69]



(10)

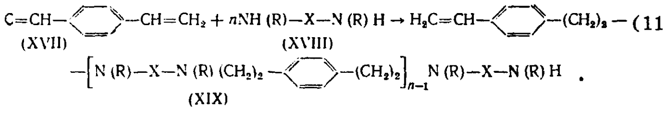
Under certain conditions, the reaction leads to the formation of polymers with 1,3-diphenylbuta-1,3-diene end groups in quantitative yield and it has been shown that the MM formed (molecular weight 50 000) are readily converted into high-molecular-weight comb polymers with anionic initiators. The photochemical reaction (10) can also proceed further, leading ultimately to polyphenylacetylene.

The relatively easy rupture of the poly(methyl methacrylate) chain on mechanical treatment has also been used to synthesise products resembling MM.[70] Ultrasonic treatment in benzene in the presence of *p*-divinylbenzene and subsequent deactivation of the system with methanol result in the formation of MM with molecular weights in the range 130 000–230 000 and functionalities of 2.2–12.0. They possess a broad molecular weight distribution and are highly inhomogeneous as regards functionality. Copolymers with styrene and methyl methacrylate have been obtained from them.[70]

2. Polyaddition and Polycondensation

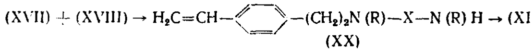
There is a very limited number of examples of the application of the polyaddition and polycondensation reactions for the synthesis of MM. The point is that in the majority of processes of this type, the lengthening of the polymer chain is achieved by employing bifunctional monomers and the nature of the end groups is determined by statistical factors and the reactant ratio. The excess of one of the reactants or the use of a monofunctional terminating agent makes it possible to guarantee with a high degree of accuracy the nature of only the two end groups. These methods are hardly used in the synthesis of monofunctional MM.

An apt example, which indicates the new possibilities which have appeared in this field, is provided by the catalytic polyaddition with participation of secondary diamines and divinylbenzene:[71,72]



(11)

The first stage in scheme (11) is rapid and quantitative. The residual vinyl group is then highly passivated, as a result of which it is possible to achieve the preliminary synthesis of the stoichiometric adduct (XX) and its subsequent poly-addition:



(12)

Analysis of the resulting polyamine MM by gas–liquid chromatography and ^{13}C NMR[71] indicates molecular weights in the range 1800–6600, which corresponds to degrees of conversion of 0.84–0.93 in reaction (11).

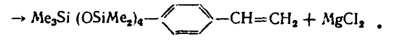
Reactions of types (11) and (12) can be used also for the introduction of various groups, for example, crown ethers, into the macromolecule, which has been used successfully in one investigation.[73]

Polycondensation has not so far provided examples of the synthesis of MM.

3. The Reactions of the Functional Groups of Macromolecules

It is possible to obtain MM by the quantitative replacement of any end group by one capable of polymerisation. Such a reaction requires the activation of the group to be substituted by the use of a reactive agent for the introduction of functional groups, so that the method involving the deactivation of living polymers is in this sense more natural. On the other hand, in the methods based on the modification of the end groups, it is possible to use a much greater range of reactions. The main requirement which they must meet is complete conversion.

Historically, the first example of the synthesis of MM refers to precisely this field. In 1962 Greber and Reese[3] achieved the reaction



and obtained polydimethylsiloxane MM in ~50% yield, which were then copolymerised with styrene.

Subsequently a number of communications concerning the introduction of a wide variety of polymerised fragments by the reaction of end groups with the corresponding agents for the introduction of functional groups were published. One of the convenient methods for the introduction of such functional groups is the use of poly(ethylene glycols) (PEG) and its monofunctional analogues, whose hydroxy-groups are readily activated. In particular, the synthesis of oligoacrylate esters, widely used for the synthesis of three-dimensional polymers, is based on these reactions.[74]

There is no doubt that the attempt to obtain monofunctional MM by the same methods as a result of the selection of the corresponding stoichiometry should lead to a mixture of products. This remark applies fully, for example, to a study[75] where a number of glycols were esterified via the scheme

$$H(OC_2H_4)_nOH + HOCOCH{=}CH_2 \xrightarrow{H^+} H(OC_2H_4)_nOCOCH{=}CH_2\ ,$$

but the monofunctionality of the final product was not reliably established.

The only real possibility of the synthesis of MM involves therefore the use of the initial monofunctional polymers and the factors which determine the choice of method for the direct introduction of functional groups in the polymerisation stage of the replacement of groups in the finished polymer is the stability of the polymer chain as regards the action of the corresponding reagents and the attainment of the required functionality.

We shall consider several of the latest examples of the synthesis of MM using these reactions. Mono- and divinylethers of PEG have been synthesised with high degrees of conversion:[76,77]

$$H(OC_2H_4)_nOH + HC{\equiv}CH \xrightarrow[180°]{Na} \begin{cases} H(OC_2H_4)_nOCH{=}CH_2\ , \\ H_2C{=}CH(OC_2H_4)_nOCH{=}CH_2\ . \end{cases} \qquad (13)$$

These are of interest from the standpoint of the subsequent synthesis of macromolecules with crown ether rings in the chain. Reaction (13) is accompanied by the degradation of the main chain, as shown by the results of the chromatographic analysis, presented below, of a mixture of bifunctional oligomers with different chain lengths *n* according to the data of Mathias et al.:[77]

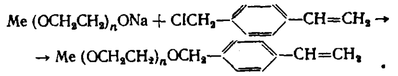
Initial PEG	Products			
	$n=2$	$n=3$	$n=4$	$n=5$
$n=3$	43%	57%	—	—
$n=4$	23%	33%	44%	—
$n=5$	—	27%	64%	8%

In this connection an assortment of milder conditions is necessary, in particular, the use of phase transfer catalysts.[76] The same approach can be applied to monofunctional polymers.

Monofunctional allyl[78] and acrylate[79] derivatives of oligoethers, i.e.

$$Ar(OCH_2CH_2)_nONa + HOCOCH{=}CH_3 \rightarrow Ar(OCH_2CH_2)_nOCOCH{=}CH_2\ , \qquad (14)$$
$$Ar = C_9H_{15}C_6H_4,\ Ph$$

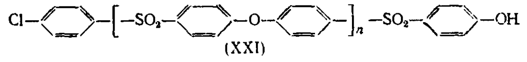
as well as their styrene derivatives,[79] i.e.



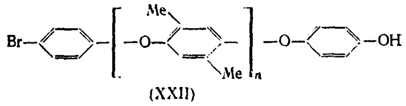
have been obtained by analogous methods, i.e. by the activation of hydroxy-groups with alkali metals.

Detailed analysis of the acrylate MM formed by capillary gas chromatographic and high performance liquid chromatography yields the distribution of the MM with respect to chain lengths but at the same time an appreciable amount of the initial school is detected, which shows that reaction (14) does not go to completion.

Fundamentally new types of MM have been obtained recently by the introduction of functional groups into polyethersulphone (XXI) and poly(2,6-dimethyl-1,4-phenylene oxide) (XXII):[80]

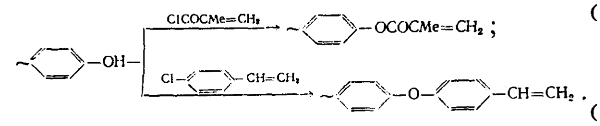


(XXI)



(XXII)

The method of synthesis of the polymers ensured in both cases the presence of one phenolic end group, which was then converted into methacrylate or styrene groups in accordance with the schemes:



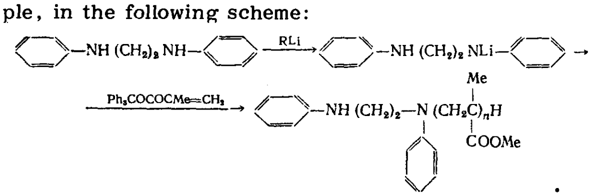
(15)

(16)

Reaction (15) was carried out in the presence of 4-*NN'*-dimethylaminopyridine and triethylamine and reaction (16) was carried out under phase transfer conditions.

The initial polymers (XXI) and (XXII) as well as the MM based on them have been investigated in detail by IR spectroscopy and ^1H and ^{13}C NMR. The equality of the signal intensities of the halogenophenyl and phenolic groups or the unsaturated groups demonstrates the presence of the planned MM structure. The complete absence of absorption due to the OH groups in the terminal phenolic fragments in the IR spectra demonstrates additionally that the introduction of functional groups is complete.[80]

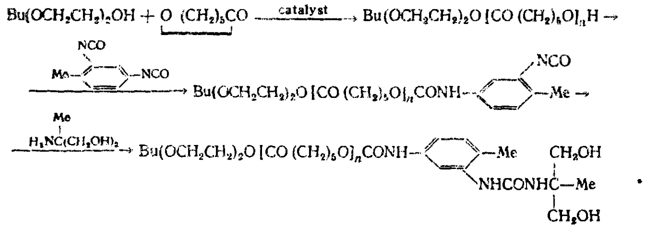
One may quote the example of the synthesis of poly(methyl methacrylate) optically active MM[81] as an example of the wide variety of the possibilities and prospects for the synthesis of MM. Such MM are of undoubted interest as the starting materials for the creation of chiral sorbents and chromatographic phases. The polymerisation of racemic triphenylmethyl methacrylate on treatment with lithium initiators in the presence of chiral diamines leads to polymers having high optical activities with different signs—$[\alpha]_D$ ranges from −354° to +194°. The end groups of the polymers are determined by the initial lithium amide initiator, for example, in the following scheme:



(XXIII), $n = 45$

The subsequent reaction of compound (XXIII) via the N–H bond with methacryloyl chloride leads to a MM whose acrylamide end groups have been clearly identified by IR spectroscopy. These MM copolymerise with methyl methacrylate via a radical mechanism.

In a number of instances the specific synthesis of MM presupposes special regulation of the nature of the end group already in the stage involving the formation of the polymer in order to be able to replace it subsequently. One of the illustrations of this approach may be provided by the synthesis of the MM from ε-caprolactone:[82]



The MM obtained can enter into polyaddition reactions via the two hydroxy-groups in the terminal fragment. They are used to synthesise modified polyurethanes.

Having completed the consideration of the problems of the synthesis of MM, we may note that in recent years a set of methods have been devised for the introduction of polymerisable groups (mainly styrene and acrylate groups) into macromolecules of different types both directly in the stage of their synthesis and via secondary reactions. The methods involving the deactivation of living polymers lead to MM with the highest functionalities. In those cases where this procedure is impossible, good results can be achieved with the aid of reactions via the end groups but here too the feasibility of the quantitative introduction of the corresponding group (or groups) must be inherent in the precursor polymer.

III. POLYMERISATION OF MACROMONOMERS

It has been assumed *a priori* that the capacity of MM for polymerisation and copolymerisation with other monomers must be complicated by a number of factors. The impossibility of achieving high MM concentrations in the reaction medium as a result of their high molecular weight should be regarded as the first although the most trivial of these. The low MM concentrations can in the first place give rise to thermodynamic prohibitions of polymerisation, particularly in those cases where the polymeric substituent is attached directly to the double bond, which as a rule decreases sharply the heat of polymerisation. Under homopolymerisation conditions, this factor should reduce the rates and average degrees of polymerisation of MM and the MM copolymerisation processes always proceed for this reason under conditions where there is an excess of the "small" comonomer. The second factor is diffusion-dependent limitations, which in the given instance extend also to chain propagation via the reaction between the macromolecules.

The polymeric substituent can naturally exert a strong steric and polar influence on the reactivity of the double bond. In this sense the MM with styrene and acrylate groups are most preferred especially if the polymer chain is on the periphery, i.e. in the benzene ring or in the ester fragment respectively.

Finally, one must reckon with the possible instability of the polymer chains of the MM in relation to the active centres propagating the polymerisation. For example, polyoxyethylene is known to exhibit a tendency to be cleaved by radical, cationic, and even anionic agents. The polymer chains of MM based on lactones and siloxanes, in which chain dissociation and macrocyclisation reactions take place readily, cannot be regarded as fully stable in relation to ionic initiators. Because of these causes, the tendency to introduce into the MM groups capable of polymerisation via a radical mechanism predominates.

Purely polymeric effects, such as, for example, the matrix influence of the MM chain on the growth of new macromolecules (the orientation of the monomers and their polymerisation in the bound state, the formation of stereocomplexes, and other matrix growth mechanisms) as well as the thermodynamic incompatibility of the initial and final chains, which may be manifested both by the segregation into separate phases and by purely kinetic effects, are also possible.

All these complications occur to some extent in processes involving MM. For example, the MM formed via the chain transfer mechanism in the radical polymerisation of methyl methacrylate[63] does not copolymerise directly with the initial monomer apparently owing to steric hindrance and thermodynamic prohibition. The characteristic features of the kinetics of the polymerisation of poly(tetrahydrofuran-styrene) MM and the low chain lengths of the polymers obtained can be accounted for by the low concentration of the MM.[83] The copolymerisation of acrylic acid with polyoxyethylene-methacrylate proceeds in a significantly different manner in the pH ranges corresponding to the comonomers bound in a complex or in a free state.[84]

The kinetics and thermodynamics of the homopolymerisation of MM have, however, been so far investigated to an extremely insignificant extent, which precludes a more detailed analysis of the above features of these processes. Much more attention has been devoted to the copolymerisation of MM, because it is the main pathway to polymers of practical interest.

1. Copolymerisation With Participation of Macromonomers

Copolymerisation is the main procedure in the synthesis of polymers based on MM. Radical initiation is regarded as the most preferred in view of its universality. The usual equation for the composition of the copolymer of a "small" monomer (M_1) with a macromonomer (M_2) has to be modified because of the low concentration of the MM:[85]

$$\frac{d[M_1]}{d[M_2]}=\frac{[M_1]}{[M_2]}\cdot\frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]}\simeq r_1\frac{[M_1]}{[M_2]}\ ,$$

which corresponds to the case of the so called "ideal" copolymerisation ($r_1r_2 = 1$) and leads to a simple kinetic equation:

$$r_1=\ln(1-\alpha_1)/\ln(1-\alpha_2)\,, \tag{17}$$

where α_1 and α_2 are the degrees of conversion of the monomers M_1 and M_2 respectively. This evidently simplifies the determination of the reactivity of the monomer M_1, but hinders and frequently altogether precludes the determination of the reactivity of the MM. The copolymerisation of MM has beeen analysed by gas–liquid chromatography.[86]

It is also easy to show that only single MM units should be incorporated in the chain during copolymerisation. Indeed, the probability of the formation of the diad M_2M_2 and hence its fraction in the comonomer

$$f_{M_2M_2}=r_2\frac{[M_2]}{[M_1]}\left(1+r_2\frac{[M_2]}{[M_1]}\right)^{-2}\simeq r_2\frac{[M_2]}{[M_1]}$$

are very small and the following probabilities can be obtained for the average block lengths:

$$\bar{p}_1=1+r_1\frac{[M_1]}{[M_2]}\gg 1\ ;$$
$$\bar{p}_2=1+r_2\frac{[M_2]}{[M_1]}\simeq 1\ .$$

In other words, the copolymerisation considered is as a rule close to statistical copolymerisation and the variation of the constants r_1 and r_2 rarely alters this situation, because the aim of the tactics employed is usually to make sure that the polymerisable groups of the MM have structures identical to that of the "small" comonomer.

Table 4 presents the copolymerisation constants for systems with participation of MM. In the main, they refer to the "small" comonomer and in this case we obtain information about the reactivity of the MM, because

$$1/r_1 = k_{12}/k_{11} \qquad (18)$$

is the ratio of the rate constants for the addition of the MM and the "small" comonomer to the radical of the latter. The quantities r_2 are of great interest from the standpoint of the analysis of the complications caused by the macromolecular nature of the MM, but they are known only in rare cases.

Table 4. The reactivities of monomers in radical copolymerisation processes with participation of MM.

MM (M_2) *	Comonomer (M_1)	r_2**	r_1**	Refs.
Poly(ethylene oxide)-styrene	Styrene	1.04 (1.00)	1.18 (1.00)	[87]
"	Butyl acrylate	0.60 (0.48)	0.11 (0.15)	[87]
Poly(ethylene oxide)-methacrylate	Styrene	0.46 (0.46)	0.41 (0.52)	[88]
Polystyrene-methacrylate	Styrene	—	0.61 (0.66)	[89]
"	Butyl acrylate	—	0.82 (0.35)	[89]
Polyisobutylene-styrene	Styrene	—	1.2—6.6***	[90]
"	Methyl methacrylate	—	0.48—0.58****	[90]
Polyvinylpyridinemethacrylate	Butyl acrylate	—	8.3	[91]
Polydimethylsiloxane-styrene	Styrene	—	1.1 (1.0)	[92]
"	Methyl methacrylate	—	0.60 (0.52)	[92]

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*The first part of the name of the MM refers to the chain structure and the second to that of the end group.

**The values for low-molecular-weight models are given in brackets.

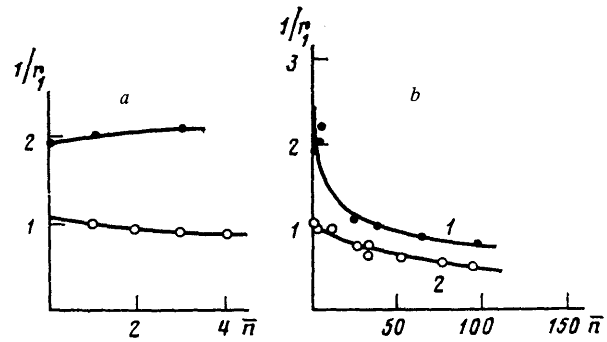
***When the MM chain length is varied.

****When the solvent is varied.

The data in Table 4 demonstrate in the first place the absence of any appreciable polymeric effects in copolymerisation, because in most cases the constants r_1 are close to those characteristic of the same pairs of low-molecular-weight monomers (indicated in brackets in Table 4) and the same applies to the few values of r_2 in Table 4. Systems where microphase separation occurs in consequence of the incompatability of the MM macromolecules and the polymer obtained are an exception. This applies to a considerable extent to, for example, copolymerisation of the polyisobutylene-styrene MM with styrene and methyl methacrylate.[90] A particularly marked effect is exerted by the increase of the molecular weight of the MM (from 4200 to 48 000), which leads to an increase of r_1 from 1.2 to 6.6 in the copolymerisation with styrene; in the latter case the reaction mixture is appreciably opalescent. Similar phenomena have been observed also in other systems.[27, 88]

The incompatibility of the polymers may play an even greater role in emulsion copolymerisation, because in this case there is a possibility of the formation of several phases and the rate of diffusion of the MM may prove to be the decisive factor. In particular, it has been shown that the emulsion copolymerisation of styrene with the polyisobutylene-styrene MM takes place with formation of the graft copolymer only in monomer drops, while the usual variant leads to polystyrene and the MM which failed to react.[93]

In the absence of explicit phase separation, the antagonism between the macromolecules of the growing polymer (consisting mainly of M_1) and the MM may be manifested by certain kinetic effects. Ito et al.,[88] who investigated in detail the dependence of the reactivity of poly(ethylene oxide) MM on the chain length (see Figure) tend towards this view. It can be seen from Fig.*a* that, in the region of short chains, there is virtually no dependence of n_1 on chain length, which indicates an insignificant inductive and steric influence of the substituent on the reactivity of the polymerisable group in the MM. In the region of great chain lengths (up to 10^2) (Fig.*b*), a monotonic decrease of $1/r_1$ is observed, which most probably indicates the corresponding decrease of the reactivity of the MM in relation to the growing macromolecule, i.e. a decrease of k_{12} in Eqn.(18). These changes are attributed to the kinetic effect of the excluded volume in intermacromolecular reactions. However, quantitative agreement with the theory of this effect has not been obtained and the idea of macromolecular antagonism has been formulated.[88]



The reactivities of poly(ethylene oxide) MM of different lengths ($\bar{n}$) in the radical copolymerisation with styrene (M_1);[88] MM with methacrylate (curves *1*) and *p*-vinylbenzyl (curves *2*) end groups.

It is essential to note that, overall, the approach to the study of the problem of the reactivity of the end groups in polymers via the investigation of the copolymerisation of MM is perhaps more correct than analysis of the processes involving the conversion of telechelate polymers into network polymers.[4] The theory of copolymerisation has been developed in detail, which makes the first approach even more justified.

On passing to the ionic copolymerisation of MM, which has not so far been touched upon, solvation interactions, matrix effects, etc. should be manifested to a considerable extent.

IV. APPLICATIONS OF MACROMONOMERS IN POLYMER ENGINEERING

The synthesis of graft copolymers clearly predominates in the preparative applications of MM. Strictly speaking, this field as a whole arose owing to the need to combine in a single macromolecular system at least two different frequently opposite properties, which cannot always be achieved by methods involving the successive copolymerisation of different monomers and block or graft copolymerisation. In graft polymers, there is a possibility of significantly different ratios of the main and grafted chains. The relatively greater freedom of the latter compared with the corresponding fragments in block copolymers leads in many instances to more favourable conditions for microphase separation, which results in qualitatively new mechanical properties of the material.

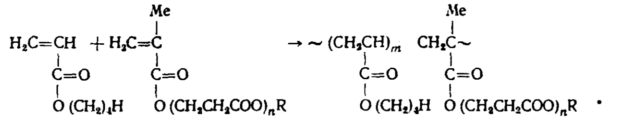
Virtually all the MM whose synthesis and polymerisation were examined in previous sections have been used to obtain graft copolymers with different "small" comonomers. The homopolymerisation of MM, leading to strictly regular comb polymers, has attracted significantly smaller and purely theoretical interest, although it is evident that in this sense the MM method is promising for the formation of liquid crystal materials.

We shall now consider the principal trends in the synthesis of graft copolymers based on MM.

It is known that the introduction of a rubber-like phase into plastics (polystyrene, materials based on epoxy-resins) increase their impact strength. A fundamentally new procedure has been proposed by Kennedy and Lo,[93] who achieved an increase by a factor of 2.5 of the impact strength of polystyrene by introducing into the latter, in the formation stage, approximately 10% of grafted polyisobutylene fragments, using the appropriate MM. The microphase separation and the enhancement effect were observed only for MM with relatively high molecular weights ($\bar{M}_n = 5 \times 10^4$). According to the authors,[93] an advantage of this method over the traditional introduction of rubbers (usually polybutadiene) is the high stability of the properties of the material as a function of time, including its stability in relation to the action of natural factors, for example, UV irradiation. The results of this study can hardly be regarded as final and it leads to new prospects for the solution of problems of this kind.

Another physicomechanical modification procedure, which is the direct opposite as regards the results achieved, involves the introduction of crystallisable fragments into elastomers. Microphase separation leads in this case to the formation of thermally reversible cross-links and to materials of the type of thermoelastoplastics. Polymeric fragments based on lactones, which are highly crystalline and give rise to a high rate of formation of the given phase, are of great interest in this connection. Their use in block copolymers is known.[94,95]

The graft copolymers of poly-β-propiolactone with butyl acrylate were first synthesised recently[18] via MM using the scheme



$$H_2C{=}CH(C{=}O)O(CH_2)_4H + H_2C{=}C(Me)(C{=}O)O(CH_2CH_2COO)_nR \rightarrow \sim(CH_2CH(C{=}O)O(CH_2)_4H)_m\,CH_2C(Me)(C{=}O)O(CH_2CH_2COO)_nR\sim \; .$$

They do indeed have the properties of unfilled acrylate rubbers. The copolymers obtained by treatment with AIBN have molecular weights in the range 30 000–60 000 and contain 46–80 wt.% of the ester fragments of poly-β-propiolactone, which corresponds on average to 1.7–3.5 grafted chains per macromolecule. In terms of their mechanical properties—strength and elongation on rupture (12 MPa and 380% respectively)—these materials approach filled rubbers based on butyl acrylate (12 MPa and 250% respectively). The properties of thermoelastoplastics based on the above MM are fully restored after the "fusion–crystallisation" cycle and have attracted evident interest.

A number of examples of the directed modification of traditional polymeric materials by means of the macromonomer techniques have been described in a recent communication by Milkovich,[1,27] who is undoubtedly a pioneer in this field. He employed polystyrene MM with methacrylate groups having molecular weights ranging from 11 000 to 16 000. The copolymers of such MM with ethyl and butyl acrylates, obtained in solution or in suspension, exhibit markedly the properties of reinforced rubbers with microphase separation, in which the rigid polystyrene domains simulate a solid filler. The majority of the copolymers are thermoplastic and their mechanical properties improve significantly when subjected to shearing influences, for example, extrusion, apparently as a result of the creation of a more homogeneous physical network. The principal mechanical characteristics of a series of ternary MM copolymers (molecular weight 16 × 10^3) with a 1 : 1 mixture of ethyl and butyl acrylates according to Milkovich's data[1] are given below:

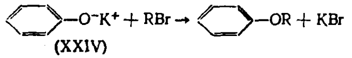
MM content, wt.%	25	30	40	45	50
Yield point, MPa	—	1.9	8.3	12.4	18.0
Tensile strength, MPa	9.0	11.7	15.2	17.2	20.7
Limiting elongation, %	730	550	400	350	240

With increase of the content of MM, the copolymers undergo a change in a set of properties, being converted from thermoplastic elastomers capable of effective recovery of properties (20–30% MM) to flexible thermoplastic materials with high yield points and tensile strengths (35–45%) and finally to thermoplastic materials capable of being moulded and having a high tensile strength (45–55%).

The introduction of polystyrene MM into polyacrylonitrile (10 and 50 wt.% of the MM) makes it possible to improve significantly the conditions for the formation of films by casting methods at 150 °C. Positive effects following the introduction of MM have been observed also in the properties of poly(vinyl chloride).[27]

Other types of studies involving graft copolymers are associated with imparting various specific properties to materials. Many heterochain polymers are known to exhibit a high solvating power in relation to cations[96,97] and they are therefore used widely, together with crown ethers, as sorbents, solubilising additives, phase transfer catalysts, etc. Polyoxyethylene is perhaps of greatest interest and there have been a number of studies designed to produce the appropriate materials on the basis of its MM.[98,99]

Cross-linked polymeric sorbents based on network styrene—divinylbenzene copolymers, containing free suspended polyoxyethylene chains, have been obtained using MM.[98] It is possible to overcome in this way the low mechanical stability of the cross-linked polyoxyethylene, which precludes its direct employment as a chromatographic sorbent. The solvating power of network graft copolymers, containing different amounts of MM, have been studied in relation to the Williamson reaction



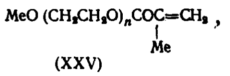
(XXIV)

R = n-Bu, C_7H_{15} . (19)

This reaction is extremely sensitive to the solvation of the cation and the ion pair (XXIV) and this is why it has become the traditional kinetic test for the solvating power of the medium.[96,100,101]

The pattern in the activation of reaction (19) by a cross-linked polymeric catalyst and also by analogous graft copolymers proved to be extremely complex. In the case of networks, the activation effect depends on the content of the MM, the degree of cross-linking, the porosity, and also the degree of swelling of the polymer and its thermodynamic compatibility with the medium and the alkyl bromide. In particular, the maximum in the dependence of the rate of reaction on the content of the MM in the network, which occurs at 5 mole %, has been attributed[98] to the character of the distribution of the reactants in the network polymer–liquid phase system. Overall, this interesting study[98] merely leads to a new approach to the synthesis of phase transfer catalysts based on polyoxyethylene, without solving the many other problems in this field.

The ability of systems of this kind to immobilise the corresponding reagents has been demonstrated in relation to gels obtained from MM of type (XXV) and methyl methacrylate with addition of 3–5% of cross-linking agents:[99]



$MeO(CH_2CH_2O)_nCOC(Me){=}CH_2$,

(XXV)
$n = 4-7$.

In the swollen state, such gels are optically transparent, which permits a spectrophotometric study of the degree of binding by the latter of alkali metal picrates as a convenient model (see, for example, Arkhipovich et al.[102]), and also of the state of the latter in a polymeric solvating medium. Experiments have shown that the equilibria

$$\text{gel} + \text{PiNa} \overset{K_1}{\rightleftarrows} \text{Gel.PiNa},$$

$$\text{gel.PiNa} + \text{glyme} \overset{K_2}{\rightleftarrows} \text{gel} + \text{glyme.PiNa}$$

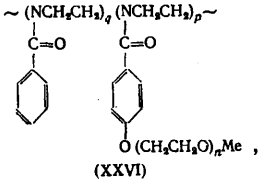
in dioxan and chloroform are strongly displaced towards sodium picrate (PiNa) immobilised in the network. The constants K_1 and K_2 proved to be ~300 litre mol^{-1} and 0.1–0.4 for networks based on MM of type (XXV) and glymes of similar length; the constants change somewhat as the chain length is altered.

These data indicate the higher solvating power of glymes in the polymer than in solution, although this is hardly likely to be achieved owing to cooperative effects, because glymes with this chain length are themselves fairly effective solvating agents.[103,104]

Spectroscopic studies[99] of the state of picrates in gel films have also confirmed the high level of solvation, because the spectra obtained correspond to solvate-separated ion pairs; the wavelengths of the absorption maxima are 368, 374, 377, and 378 nm for Li^+, Na^+, K^+ and Cl^+ respectively after the removal of the solvent. It has been suggested that the gels obtained and other analogous gels are promising for the study of the reactions of the reagents with the state solvated by macromolecules.

One of the important applications involves the creation of effective surfactants using MM. Comb polymers with a hydrophilic base and hydrophobic grafted chains (and conversely) have been used fruitfully for a long time for the steric (antropic) stabilisation of various dispersions, emulsifications, etc. (see, for example, Barrett[105]), but the approach using MM greatly simplifies the formation of such substances and extends the range of the possible structural variants. Polymers of this type are also of interest for the modification of the surfaces of polymeric materials and the solution of the problem of their compatibility. There have been several studies illustrating these possibilities.[92,106–109]

Using polyoxyethylene MM of types (IV) and (V), Kobayashi et al.[106] synthesised graft copolymers with the structure (XXVI):



(XXVI)
$n = 19-43$.

Owing to the presence of hydrophilic (polyoxyethylene) and hydrophobic (polyphenyloxazoline) fragments, these copolymers exhibit a high surface activity at the air–water interface. The surface tensions (γ, dn cm^{-1}) of water and 1% solutions at 28.5 °C are given below:

Water	71.4
MM	56.9
MM homopolymer ($p = 3$)	54.8
The copolymer (XXVI) ($p/q = 1:8.5$)	28.8

It has been suggested that these non-ionogenic surface-active graft copolymers would prove to be effective stabilisers of dispersions and also antistatic agents when they are introduced into plastics, like the analogous block copolymers.[107]

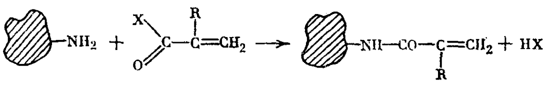
Extremely interesting and very promising surface effects have been observed after the introduction into polystyrene or poly(methyl methacrylate) films of small amounts of the corresponding graft copolymers containing hydrophilic polyamide[108] or, conversely, hydrophobic polydimethylsiloxane fragments.[92,109] Measurement of the wetting angles in water for polystyrene films obtained by casting onto glass plates has shown, for example, that the polyamide (see the footnote to Table 3) blocks are concentrated on the surface adjoining glass even when their content in the film is ~0.2%. This has been confirmed also by IR total internal reflection Fourier spectroscopic data. The surface of the film turned towards air does not differ in any way from that of the usual polystyrene.

The opposite picture has been observed for the system comprising poly(methyl methacrylate) and the graft copolymer of methyl methacrylate with polydimethylsiloxane-methacrylate.[110] In this case the siloxane blocks are concentrated on the "air" surface of the film, rendering it markedly hydrophobic; cos θ, where θ is the wetting angle, changes from 0.5 to −0.2 when not more than 0.5 wt.% of the siloxane component is introduced. The other surface of the film is also somewhat enriched in the graft copolymer and its distribution with respect to the thickness of the film follows clearly from IR reflectance spectroscopy. This effect, caused by the macroscopic separation of the copolymer in the bulk phase, is extremely stable and is almost fully retained after prolonged washing of the surface with n-hexane—an effective solvent for polydimethylsiloxane. In the case of similar modification of surfaces by static or block siloxane copolymers and also siloxane homopolymers, such washing eliminates the hydrophobic effect almost completely.

Presumably the application of biphilic graft copolymers constitutes a promising means of influencing the compatibility of polymers in composites, the character and stability of the microphase separation, and the modification of polymer films and fibres.

The biphilic property is one of the main qualities of graft copolymers widely used in the synthesis of biomedical materials. By virtue of MM, a series of new approaches have been discovered in this field also.

Plate and co-workers[111–113] have been consistently developing the immobilisation of biologically active compounds (BAC)—proteins, enzymes, etc.—on macromolecules or in cross-linked hydrophilic gels via intermediate "macromonomers". The principle of the method consists in the synthesis of MM by the acylation of BAC, i.e.



(BAC) (XXVII)

and the subsequent copolymerisation of the resulting acrylamide MM with an appropriate comonomer in the absence or presence of a cross-linking agent. It is possible to graft compound (XXVII) to various materials, for example, under the influence of γ-radiation. The functionality of the MM (XXVII) naturally depends on the number of the initial amino-groups in the BAC and on the degree of their substitution, which has been considered in detail in novel studies by this group of workers (see the review of Plate et al.[112]).

An important condition for the attainment of the final aim is the retention by the BAC of its activity at all the stages of the immobilisation process. It has been shown in relation to human serum albumin[113] and a number of other proteins that the BAC retain their secondary structure and that their binding centres are unaffected on modification.

The approach considered made it possible to create new effective sorbents for biospecific chromatography and materials with improved haemocompatibility, which is adequate even for making artificial veins. An important consequence of these studies is also clear-cut correlations between the haemocompatibility of the polymer and the effectiveness of its action on the clotting system of blood.

Another application concerned with the creation of biomedical materials, employing purely synthetic MM, has also been developing effectively.[17,73,114-116] The introduction of polyaminoacid, polyamine, polyamide, and also polysaccharide fragments, exhibiting "biological" affinity, into the usual polymers, most often polystyrene, which plays the role of an inert hydrophobic carrier, makes it possible to obtain two-phase materials which constitute the base for the creation of biosorbents, specific membranes, and anticlotting coatings.

The problem of the separation of *B*- and *T*-lymphocites, which is one of the key problems in modern chemical immunology, has attracted much interest recently.[117] The materials created on the basis of MM exhibit a high selectivity in such separation and are being studied vigorously. The selectivity coefficients A_B/A_T of the adsorption of the corresponding cells on polystyrene and graft copolymers with polyaminoacids [see Scheme (3)] and polyamine fragments (XIX), based on the results of several studies,[114-116] are presented below:

Polystyrene (PS)	—	1.18
PS with grafted polyaminoacid	(26%)	1.54
Ditto	(50%)	2.15
PS with grafted polyamine	(9%)	4.47
Ditto	(15%)	2.89
"	(25%)	2.45
"	(50%)	3.16

The mass content of the graft copolymers is indicated in brackets. Their selectivity is frequently antagonistic to the overall absorption of lymphocites on columns of this type.[115] However, the latest estimates have shown that the population of *T*-lymphocites can be obtained in yields up to 50% and with a purity of approximately 95% (for example, by employing the copolymer of polystyrene with a 9% content of polyamine). For this purpose, the columns are additionally modified by proteins, for example, albumin[115] or additives regulating the hydrophilic properties of the material.

Overall, the biomedical applications of MM have been developing most vigorously in recent times.

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Thus a new field, which has significantly enriched synthetic polymer chemistry, has arisen among reactive oligomers and has been developing vigorously. The use of MM containing one polymerisable end group, frequently an unsaturated group, made it possible to obtain a number of fundamentally new comb and graft polymers. Methods for the introduction of functional groups—initiation and deactivation in ionic polymerisation and radical telomerisation—have been developed in detail. The first reviews of studies in this new field have already appeared.[118,119] Presumably this field and also the synthesis of block copolymers, developing in parallel, will serve as sources of new polymeric materials for various purposes.

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Some Problems of the Development of the Physicochemical Principles of Modern Extraction Technology

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The latest advances in the quantitative prediction of the influence of the composition of the aqueous and organic phases, the nature of the functional groups of the extractants and the substituents attached to these groups, and the nature of the diluent on the position of extraction equilibria in the extraction of various metals are examined. The influence of these factors on the selectivity in the separation of different elements as well as elements with similar properties and on the possibility of the far reaching removal of impurities comprising weakly extractable elements from the element to be extracted is analysed and their influence on the properties of extraction systems, as determined by the interfacial tension, is estimated. It is shown that the corresponding quantitative prediction can be made with adequate accuracy for a wide range of systems on the basis of equations derived from linear free energy relations and the tabulated parameters ID, ID*, ΔG^*_{hydr}, etc., obtained by statistical treatment of the available extensive sets of extraction data, as well as the parameters σ^*, σ_φ, E^*_S, H, etc. known in physical organic chemistry. The ways of applying the methods for the prediction of extraction equilibria in combination with mathematical modelling to the optimisation of the structure and regimes of technological extraction schemes are considered. The bibliography includes 182 references.

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I. INTRODUCTION

During the latest decades, extraction has come to be used in industry as the basis for the technological schemes whereby rare and radioactive elements as well as certain non-ferrous metals can be obtained and separated. With an appropriate choice of components of the organic phase (extractants and diluents) and aqueous phase (acids and salts), this procedure permits the selective extraction of the required individual elements from complex mixtures.

The aim of scientific research in the field of extraction technology is the selection of optimum conditions ensuring the most complete extraction and separation of the elements as far as possible with the smallest consumption of the reagents and using the simplest possible and most compact equipment. An important question in this connection is the creation of waste free or low waste technological schemes which require the use of extractants, diluents, and water soluble reagents whose application would not entail the contamination of the environment. In many instances ultrahigh purification of a valuable element by a factor greater than 10^6-10^8 in a small number of operations is needed.

A clear example of the exceptionally effective application of liquid extraction is its use for the extraction and separation of uranium, plutonium, and neptunium in the regeneration of spent fuel from atomic power stations whereby these valuable elements are separated from several tens of radioactive elements treated as impurities (fission products) in a relatively small number of operations and for a very small consumption of reagents. Liquid extraction is also used to extract many valuable elements from ores and other natural mixtures with a complex composition.

The extraction schemes for the processing of atomic power station fuel developed in the USSR, presented at a series of International Conferences,[1-4] are greatly superior to those described in the world literature in terms of all the parameters, for example, the purification coefficients for valuable components in a single cycle (by a factor up to 10^6). The parameters attained are to a large extent the result of the high level of development of the physicochemical principles of extraction technology. Soviet investigators have made a major contribution in ensuring a high level of research in this field.

Among the large number of problems in extraction chemistry which are of interest for the development of extraction technology, the present review deals, first, with the principles for the selection of the optimum qualitative and quantitative composition of the phases in extraction systems, and, second, with the principle for the selection of the optimum structure of the flows of aqueous and organic phases in technological schemes based on extraction.

One of the most important conditions governing such choice involves the estimation and comparison of numerous possible variants. This requires the development of ideas and models which would make it possible to predict without experiments, or after carrying out a minimal number of experiments, various properties of extraction systems of interest for technology. This is particularly important for systems incorporating radioactive elements, since experiments involving such elements are laborious. This is probably why the main advances in the field considered were made as a result of many years' work by radiochemists, although the results obtained may find and are finding extensive applications in the extraction technology of the processing of non-radioactive materials as well.

II. PREDICTION AND OPTIMISATION OF THE PROPERTIES OF EXTRACTION SYSTEMS

For the prediction of the partition coefficients of the elements D, one must bear in mind that the extraction of inorganic compounds is usually determined by the consecutive or simultaneous occurrence of two processes: (a) the reaction involving the formation of a hydrophobic compound (solvate, hydratosolvate, chelate, or salt) as a result of the interaction of the inorganic ion or compound extracted from the aqueous phase with the extractant molecules;

(b) the partition of the hydrophobic compound between the phases without the formation of new compounds and for this reason referred to as "physical partition".

We shall consider both these processes in succession.

The Formation of a Hydrophobic Compound

When the solvate of a metal salt (MA_n) or acid (H_nA) is formed as a result of solvation by the nucleophilic extractant† (S), the process can be represented schematically by equations of the following type respectively:

$$M^{n+} + nA^- + m\bar{S} \overset{K}{\rightleftarrows} \overline{MA_nS_m} \;, \tag{1}$$

$$nH^+ + A^{n-} + m\bar{S} \overset{K}{\rightleftarrows} \overline{(H_nA)S_m} \;, \tag{2}$$

where the bar denotes the compound present in the organic phase.

When a chelate of the salt of the metal extracted with a hydrophobic acid HX is formed, a cation exchange reaction described by equations of the type

$$M^{n+} + n\overline{HX} \overset{K}{\rightleftarrows} \overline{MX_n} + nH^+;\; M^{n+} + n\overline{M'X} \overset{K}{\rightleftarrows} \overline{MX_n} + nM'^+. \tag{3}$$

takes place. When the system contains a nucleophilic extractant, reaction (3) may be supplemented by the formation of a chelatosolvate in accordance with the equation

$$M^{n+} + n\overline{HX} + m\bar{S} \overset{K}{\rightleftarrows} \overline{MX_nS_m} + nH^+. \tag{4}$$

When a salt incorporating the element extracted in the form of a simple or complex anion Y^{n-} is formed, the extraction reaction is described by the equation

$$n\overline{RA} + Y^{n-} \overset{K}{\rightleftarrows} \overline{R_nY} + nA^-. \tag{5}$$

Eqns.(1)–(5) describe the fundamental basis of the main types of extraction reactions involving solvate, cation exchange, chelatosolvate, and anion exchange mechanisms. In reality, there is a possibility of more complex varieties of these processes, associated, for example, with the existence of extractants or compounds extracted in the form of associated species[6] or even micelles.[7] There is also a possibility of the hydration of the extractant or compounds extracted and of incomplete displacement by the extractant molecules of the water hydrating the compound extracted. For example, if the nucleophilicity of the extractant used in extraction in accordance with Eqns.(1) and (2) is insufficient for the displacement of water from the inner coordination sphere of the metal cation M^{n+} or the proton H^+, then extraction via a mechanism referred to as the hydrate-solvate mechanism[8] and described by equations of the type

$$[M(H_2O)_p]^{n+} + nA^- + m\bar{S} \overset{K}{\rightleftarrows} \overline{[M(H_2O)_xA_yS_z]\,A_{n-y}S_{m-z}} + (p-x)H_2O, \tag{6}$$

$$n[H(H_2O)_p]^+ + A^{n-} + m\bar{S} \overset{K}{\rightleftarrows} \overline{[H(H_2O)_x]_nAS_m} + n(p-x)H_2O. \tag{7}$$

takes place.

The incomplete displacement of water or the association of the molecules of the compound involved can also complicate reactions of types (3) and (5). However, regardless of the specific composition of the hydrophobic compound extracted, its formation via the corresponding chemical reaction, which obeys the Law of Mass Action, is essential for extraction to take place.

Partition between Phases of the Hydrophobic Compounds Formed

This process does not involve the additional formation of new compounds. For example, the partition between the phases of the solvate formed via a type (1) reaction may be described by the equation

$$MA_nS_m \overset{P_0}{\rightleftarrows} \overline{MA_nS_m} \;. \tag{8}$$

If the compound present in the aqueous phase is itself hydrophobic (without the additional incorporation in it of extractant molecules), then the extraction reduces to one process of type (8), frequently referred to as "physical" partition. The quantitative description of the equilibria (1)–(7) and (8) requires the determination of the constants K and P_0 referred to as the extraction constant and the partition constant respectively.

The Relative Contributions of the Influence of the Chemical Reaction and of the "Physical" Partition on the Extraction Equilibrium

Under conditions where the hydrophobic compound formed via reactions of type (1)–(7) passes almost completely to the organic phase, the partition coefficient D_0 may be calculated[9–13] with the aid of equations derived from the Law of Mass Action using the extraction constant K. For example, equations of the following type can be used for reactions of type (1):

$$D_0 = K[A^-]^n[S]^m \frac{(\gamma^{\pm}_{MA_n})^{n+1}(\gamma_S)^m}{\gamma_{MA_nS_m}} = K\Pi \;, \tag{9}$$

where γ are the activity coefficients of the corresponding compound and Π is the product of all the terms of Eqn.(9) which follow K.

Eqn.(9) is the limiting case of a more general equation (10), which takes into account both complex formation and partition. In the general case, where the solvate extracted is not very hydrophobic and remains partly in the aqueous phase, the measured partition coefficient D is smaller than the "ideal" coefficient D_0 calculated from Eqn.(9), and it has been shown[14] that it is related to D_0 in the following manner:

$$\frac{1}{D} = \frac{1}{D_0} + \frac{1}{P_0} = \frac{1}{K\Pi} + \frac{1}{P_0} \;. \tag{10}$$

It is readily seen that, when the solvate is very hydrophobic, i.e. when $P_0 \to \infty$, the term $1/P_0 \to 0$ and D therefore tends to $D_0 = K\Pi$ for finite values of K and D_0. This makes it possible to restrict the calculations to Eqn.(9) for the partition in such systems. Equations of type (9) are used to calculate the partition coefficients in the majority of systems of practical importance. Highly hydrophobic extractants are usually chosen for such systems (in order to eliminate losses due to their solubility in water and to reduce to a minimum the contamination of aqueous streams by the extractant), which form moderately stable complexes via reaction (1) (to facilitate both the extraction and the subsequent re-extraction).

The wide scale and successful application of Eqn.(9) sometimes has led investigators to lose sight of its special character and to use it for less hydrophobic systems, obtaining thereby results which were not fully adequate. At the same time, in the general case where stable complexes are formed via reaction (1) (i.e. K is very high), even the use of highly hydrophobic extractants may result in a value of K so high that $1/D_0$ is comparable to $1/P_0$. Account must then evidently be taken of the contributions of both terms of the right-hand side of Eqn.(10) to the real partition coefficient D. The influence of physical partition on the extraction equilibrium must be taken into account also in extraction via reactions of types (2)–(8).

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†Trialkyl phosphates, phosphine oxides, sulphoxides, carboxylic acid amides, the salts of amines and quaternary ammonium bases, and other hydrophobic compounds incorporating functional atoms having electron-donating properties and hence capable of forming coordinate bonds with electrophilic metal cations or hydrogen bonds with proton donating molecules may be classified as nucleophilic extractants.[5]

Thus in the general case the prediction of the extraction capacity reduces to the prediction not only of the constants# K but also of P_0, to which attention has been drawn.[14,15]

The Principal Approaches to the Prediction of the Quantities K and P_0

In the first stage of the selection of the optimum extraction system, one is usually guided by the familiar criteria governing the capacity of the cations, anions, and molecules of extractants for the formation of compounds via reactions (1)–(8) (in order to estimate K) and by the general ideas concerning the enhancement of hydrophobic properties with increase of the bulk of the organic part of the extractant molecule (in order to estimate P_0). However, at the stage involving more accurate optimisation, and particularly when mathematical models are used, not only qualitative but also quantitative prediction of the influence of various factors on K and P_0 is frequently necessary. In both instances the approach based on the use of the principal linear free energy relations, which has been developed in the USSR for extraction during the last two decades,[12,14,16–29] is more convenient for technological predictions. This approach is widely used in physical organic chemistry.[30–32] In the field of extraction, priority§ as regards the employment of this approach belongs to Soviet investigators. The principle of the linear free energy relations involves the employment of empirical parameters which reflect quantitatively the overall influence of various factors of the extraction equilibrium.

It is essential to note that other approaches to the description of the influence of the nature and concentration of the components of extraction systems on the extraction equilibrium are also possible and have been widely investigated. However, one can apply to the majority of the approaches discovered the apt definition put forward by Belousov and Popov,[34] formulated in the words "formally rigorous" approaches. The rigour of these approaches consists in the fact that, in the derivation of formulae relating K to the composition and nature of the components of the phases, the influence of a large number of different details of the extraction mechanism is taken into account, for example, all the complex formation equilibria (with allowance for the stability constants and activity coefficients of all the complexes formed in the aqueous and organic phases), the hydration and association equilibria of the extractant molecules[8,20,35–39] or the molecules extracted by them,[13,40,41] etc. On the other hand, the formality of the treatment consists in the fact that the "rigorous" expressions obtained, taking into account particular details of the interactions in the system investigated, usually include at the same time a series of new relations, whose form cannot so far be predicted theoretically and ultimately requires an empirical determination. For example, when account is taken of hydration, an empirical determination of the dependence of the activity of water in the aqueous phase on the concentrations of various components dissolved in it is required;[8,10,35] when complex formation is taken into account, one has to determine the activity coefficients of all the ions present in the aqueous phase[40] and of the molecules of the extractant and the compound extracted in the organic phase[41] as well as the stability constants of all the complexes formed in the system and their activity coefficients.

Without wishing to diminish in any way the cognitive importance of the "formally rigorous" approaches for a meaningful description and investigation of the extraction mechanism, one should note that, when they are applied to the practical prediction of extraction equilibria in the development of technological processes, it is usually necessary to carry out a larger volume of empirical investigations than is necessary when equations based on the principle of linear free energy relations are employed. Furthermore, the amount of experimental work essential in the "formally rigorous" approach is frequently so large that it is much simpler to measure experimentally the partition coefficients instead of predicting them theoretically. As a result of this, methods employing the dependence of the partition coefficients on various factors (to which equations have sometimes been fitted and which frequently do not take into account the details of the process mechanisms[42–44]) and simple formulae based on the principle of linear free energy relations, which achieve a combined allowance for the interaction of a large number of various details of the mechanism influencing the extraction equilibrium, are used for the prediction of technological parameters in most cases and not the "formally rigorous" approaches. The "formally rigorous" approaches to the description of extraction equilibria will probably assume ever increasing importance in the future as the theory of solutions develops and the contribution of relations predicted on fully theoretical grounds increases.

All the modern approaches to the quantitative description of extraction equilibria have been described in a monograph.[8] In the present review, devoted to the methods for the optimisation of technological extraction processes most widely used in practice, attention has been mostly concentrated on equations based on the principle of linear free energy relations. The application of these equations makes it possible to made predictions most simply and apparently with least expenditure of labour, at the present time, on experiments. The application of the principle of linear free energy relations to the prediction of the constants of the two principal equilibria indicated above (P_0 and K) is examined successively below.

1. Equilibria in Extraction Processes Not Involving the Formation of New Compounds ("Physical" Partition)

A partition of this type depends on the hydrophobic properties of the substances extracted and the overall absolute free energy of the process (and hence $\lg P_0$) increases with decrease of the absolute free energy of hydration of the partitioned compound. The influence of the increments characterising the structural components of the molecules of the partitioned compounds on $\lg P_0$ has been found to be additive for such compounds. For example, the introduction of each new CH_2 unit into the extractant molecule increases $\lg P_0$ by 0.4–0.5. A detailed scale of the increments π (Table 1),¶ characterising the structural elements and permitting the prediction[46–50] of the physical partition constants for members of each homologous series of extractants in terms of the equation

$$\lg P_0 = a + b\Sigma\pi \qquad (11)$$

The determination of the activity coefficients, which are necessary for calculations by equations of type (5), is an independent problem. The methods used for such calculations have been surveyed in a monograph.[10]

§ The history of the application of the principle of the linear free energy relations to extraction has been briefly surveyed.[14]

¶ A more detailed compilation of the parameters π may be found in a monograph.[45]

has been developed. Here a and b are coefficients which remain constants within the limits of a series of extractable substances with different structures (the nature of the aqueous phase and that of the organic solvent immiscible with it remains unchanged within the limits of the series).

Table 1. The increments π characterising the hydrophobic properties of the structural groups of the extractant in relation to physical partition.[46,47]*

Group	π	Group	π	Group	π
$-CH_2$	0.52	OH	−1.20	$-C\genfrac{}{}{0pt}{}{/\!\!/O}{\backslash H}$	−1.10
$-CH_3$	0.69	Br	1.01	$-C\genfrac{}{}{0pt}{}{/\!\!/O}{\backslash NH_2}$	−3.10
$\stackrel{\backslash}{\underset{/}{-}}N$	−2.50	I	1.30	$\genfrac{}{}{0pt}{}{\backslash}{/}C\genfrac{}{}{0pt}{}{/}{\backslash}$	0.18
$\genfrac{}{}{0pt}{}{\backslash}{/}NH$	−2.30	—COOH	−0 93	$\stackrel{\backslash}{\underset{/}{-}}CH$	0.32
Cl	0.92	—COO—	−1.01	$-NH_2$	−2.25
$\genfrac{}{}{0pt}{}{\backslash}{/}S{=}O$	(−3.8)	$\stackrel{\backslash}{\underset{/}{-}}P{=}O$	(−0.7)	$-C_6H_5$	(4.40)
HPO_3^-	(−5.2)	$\stackrel{\backslash}{\underset{/}{-}}\underset{\vert}{NH^+}$	(−3.5)	$\stackrel{\backslash}{\underset{/}{-}}PO_4$	(−0.80)

*In this and other tables, the values shown in brackets were obtained by treating limited sets of data; they may be revised as these sets are increased.

The parameters π for a series of structural elements of the partitioned compound, the elements in a pure state being capable of dissolving in an aqueous phase, vary in parallel with the variation of the free energy of hydration of these groups and linearly as a function of the empirical parameter $\Delta G^*_{\mathrm{hydr}}$ related to it (Table 2).[51,52] For this reason, for example for a series of amine salts having the same cation but different anions, the quantity $\lg P_0$ increases linearly with increase of $\Delta G^*_{\mathrm{hydr}}$ for these anions. Thus the partition of a series of tri-n-butylammonium salts with different anions between water and chloroform[54] can be described by the equation $\lg P_0 = 2.28 + 0.02\,\Delta G^*_{\mathrm{hydr}}$. For amine salts of different structure, incorporating both different cations and different anions, the partition in the system involving $CHCl_3$ can be calculated from the formula $\lg P_0 = -3.52 + 0.48n_C + 0.02\,\Delta G^*_{\mathrm{hydr}}$, where n_C is the number of carbon atoms in the alkyl chains of the amine, $\Delta G^*_{\mathrm{hydr}}$ the parameter of the hydration of the anion, and the coefficient 0.48 corresponds to π for the CH_2 group of the amine.

The changes in $\lg P_0$ occurring on changing the nature of the organic solvent in which extraction takes place for systems where the interaction between the diluent and the compound extracted has the character of non-specific solvation (without the formation of donor–acceptor and hydrogen bonds) may be predicted on the basis of the principle of linear free energy relations using the parameters ID* ("influence of the diluent")[55–57] listed in Table 3. It has been shown[55] for a large number of examples that, within the limits of each series of systems including the given partitioned compound and different diluents, $\lg P_0$ increases linearly with increase of ID* in accordance with an equation of the type $\lg P_0 = a + b\mathrm{ID}^*$.

Together with the ID* scale, one can apparently also use for the prediction of $\lg P_0$ the "polarity-polarisability" π^* scale, developed subsequently,[58] which is effectively correlated with the ID* scale. The authors,[58] who developed the π^* scale, demonstrated convincingly that it is possible to construct a scale describing the influence of non-specific solvation alone and a wide range of different phenomena.

Table 2. The average values of $\Delta G^*_{\mathrm{hydr}}$ for different anions.[53]

Anion	$-\Delta G^*_{\mathrm{hydr}}$, J mol^{-1}	Anion	$-\Delta G^*_{\mathrm{hydr}}$, J mol^{-1}
Acid phosphate ($H_2PO_4^-$)	522	Propionate	347
Hydroxide	393	Butyrate (butanoate)	338
Fluoride	381	Chloride	330
3-Hydroxybenzoate	365	Phenoxide	330
Acetate	356	Valerate (pentanoate)	329
Bicarbonate	351	Phenylacetate	324
Iodate	350	Bisulphate	323
Formate	349	*p*-Pentoxybenzoate	260
Caproate (hexanoate)	318	Fluoroborate	259
Bromate	317	4-(2-Pyridylazo)resorcinol anion	257
Benzoate	316	3-Nitrobenzenesulphonate	255
4-Hydroxybenzenesulphonate	308	4-Nitrobenzenesulphonate	255
Oenanthate (heptanoate)	306	Holdenate $[Co(C_4H_7O_2)_2(NO_2)_2^-]$	255
Bromide	303	Octanesulphonate	255
Tropaeolin O anion	303	Naphthalenesulphonate	255
Caprylate (octanoate)	295	$HgCl_3^-$	249
Nitrate	294	*p*-Hexoxybenzoate	248
Naphthoate	292	Naphthol Orange anion	247
Chlorate	291	Tropaeolin OOO anion	246
3 Nitrobenzoate	288	Perchlorate	244
Phenobarbital anion	287	$Ag(CN)_2^-$	244
4-Nitrobenzoate	287	$Hg(CN)_3^-$	243
Pelargonate (nonanoate)	286	$BiCl_4^-$	239
Benzenesulphonate	285	Erdmannate $[Co(NH_3)_2(NO_2)_4^-]$	239
Trinitrobenzoate	284	*p*-Heptyloxybenzonate	239
p-Propoxybenzoate	280	Perrhenate	239
Trichloroacetate	277	Dinitrophenoxide	234
Toluene-*p*-sulphonate	277	3-Phenylpropyl sulphate	234
1-Hydroxy-2-nitrosonaphthalene-4-sulphonate	277	*p*-Octyloxybenzoate	232
Methyl Red anion	275	Methyl Orange anion	229
2-Hydroxybenzoate (salicylate)	275	Trinitrobenzenesulphonate	228
Amobarbital anion	273	$Au(CN)_2^-$	227
3-Nitrophenoxide	273	Naphthol Yellow anion	226
Caprate (decanoate)	272	Butyl Orange anion	219
p-Butoxybenzoate	272	2-Naphthyl sulphate	218
Iodide	267	$Au(CN)_4^-$	217
Hexobarbital anion	267	Rose Bengal anion	216
Pertechnate	266	Anthracene-2-sulphonate	213
Thiocyanate	266	Bromothymol Blue anion	151
4-Nitrophenoxide	265	HgI_3^-	148
$BiBr_4^-$	207	Dioctyl sulphosuccinate	134
$HgBr_4^-$	206	$AuCl_4^-$	130
Tropaeolin OO anion	203	Hexanitrodiphenylamine anion	111
Picrate	197	Dipicrylamine anion	102
$TlCl_4^-$	191	$AuBr_4^-$	75
2,4-Dinitro-1-naphthoate	183		
Brilliant Red A anion	175		
$TlBr_4^-$	154		

This is fully consistent with the treatment, published earlier,[51] of the physical significance of the ID* scale and the ideas concerning the role of non-specific and specific solvation in extraction processes.[16,51,59] The present author and his co-workers[66] also showed that, when solvents interacting with the solute solely via the non-specific solvation mechanism are chosen, then a satisfactory linear correlation of the parameters of the π^* scale with those of a number of other scales known in organic chemistry, namely the E_T,[60] Z,[61] χ_R,[62] S,[64] θ,[65] etc. scales obtains for all these solvents. We have shown[66] that the ID* scale is well correlated with the parameters π^* and satisfactorily correlated with the parameters of the other scales indicated above for solvents chosen in this way, provided that corrections are applied for the differences between the molar volumes. A linear correlation between the ID* scale and the ε^0 scale[68] has been established.[67]

Table 3. The parameters ID*, π^*, and lg k_i of the diluents*.[66]

Solvent	ID*	π^*	lg k_i
Alkanes			
Decane	—1.1	—	—
Octane	—0.9	—	—
Isooctane(2,2,4-trimethylpentane)	—0.8	—	—
Heptane	—0.6	—0.08	—
Hexane	—0.4	—0.08	—5.0
Halogenohydrocarbons			
Perfluoro-n-heptane	—2.3	—0.39	—
Perfluorodimethyldecalin	—1.3	—0.33	—
Tetrachloroethylene	1.1	—	—
Carbon tetrachloride	1.4	—	—
1-Chlorohexane	2.0	—	—2.11
1,1,1-Trichloroethane	2.0	0.49	—
trans-Dichloroethylene	2.1	0.44	—2.3
1-Chlorobutane	[2.2]	(0.39)	—1.89
1-Bromobutane	[2.2]	—	—1.89
Trichloroethylene	[2.3]	0.53	—2.04
Trichlorobenzene	2.4	0.71	—1.15
Pentachloroethane	[2.5]	(0.62)	—1.48
Bromobenzene	2.5	0.79	—1.05
Iodobenzene	2.5	0.81	—0.89
1,2-Dibromoethane	2.6	0.75	—0.89
Fluorobenzene	[2.6]	0.62	—
Bromoethane (ethyl bromide)	2.7	—	—1.62
m-Dichlorobenzene	[2.5]	0.67	—1.46
o-Dichlorobenzene	2.7	0.80	—1.0
1,2,4-Trichlorobenzene	2.8	—	—
1,1-Dichloroethane	[3.0]	—	—1.12
1,4-Dichlorobutane	[3.2]	—	—0.72
cis-Dichloroethylene	[3.2]	—	—0.85
1,2-Dichloroethane	3.5	0.81	—0.42
1,1,2-Trichloroethane	[3.5]	—	—0.48
1,1,2,2-Tetrachloroethane	[3.7]	0.95	—0.06
Dichloromethane (methylene chloride)	4.0	0.82	—0.55
Bromoform	4.0	—	—0.55
Dibromomethane (methylene bromide)	[4.1]	(0.92)	—
Chloroform	4.5	0.58	—0.89
Diiodomethane (methylene iodide)	[4.6]	(1.12)	—
Nitrogen-containing hydrocarbons			
Tributylamine	[—0.5]	0.16	—
Triethylamine	[0.3]	0.14	—
Benzyldimethylamine	[1.4]	0.49	—
2,6-Dimethylpyridine (mutidine)	[2.8]	(0.80)	—
NN-Dimethylaniline	[3.1]	0.90	—
Quinoline	[3.3]	(0.92)	—
4-Methylpyridine	[3.3]	(0.84)	—
Propionitrile	[3.4]	0.71	—0.55
Benzonitrile	[3.5]	0.90	—0.41
Phenylacetonitrile	[3.6]	0.99	—
Pyridine	[3.7]	0.87	—
Nitroethane	[3.7]	—	—0.34
Acetonitrile	[3.9]	0.75	—0.33
Nitrotoluene	4.1	—	—
Nitromethane	[4.2]	0.85	0.04
Nitropropane	4.3	—	—0.54
Nitrobenzene	4.3	1.01	—0.32
Ethers, esters, and ketones			
Diisopropyl ether	[0.7]	0.27	—
Dibutyl ether	0.8	0.24	—3.4
Di-n-propyl ether	[0.8]	(0.27)	—
Trimethyl orthoacetate	[1.2]	0.35	—
Diethyl ether	[1.3]	0.27	—2.92
Butyl acetate	[1.5]	0.46	—
Diethyl carbonate	[1.6]	0.45	—
Ethyl propionate	[1.9]	(0.47)	—
Diethyl malonate	[1.9]	0.64	—
Ethyl acetoacetate	[2.0]	0.61	—
Ethyl trichloroacetate	[2.0]	0.61	—
1,2-Dimethoxyethane	[2.1]	0.53	—
Diphenyl ether	[1.9]	0.66	—1.37
Dibenzyl ether	[2.1]	0.80	—
Ethyl benzoate	[2.6]	0.74	—1.08
2-Butanone	[2.9]	0.67	—1.01
Cyclohexanone	[3.0]	0.76	—0.8
Propylene carbonate	[3.1]	(0.83)	—
Cyclopentanone	[3.2]	0.76	—0.66
4-Phenyl-2-butanone	[3.3]	—	—0.48
Phenylpropanone	[3.4]	—	—0.48
Hexane-2,5-dione	[3.4]	—	—0.46
Acetophenone	[3.4]	0.90	—0.38
Aromatic and cyclic hydrocarbons			
Cyclohexane	0.5	0.0	—4.15
Cyclohexene	[0.7]	—	—3.7
Triethylbenzene	0.95	—	—
Butylbenzene	1.3	—	—
Mesitylene	[1.4]	0.41	—2.62
Isobutylbenzene	1.4	—	—
Trimethylbenzene (pseudocumene)	1.45	—	—
Isopropylbenzene (cumene)	[1.5]	0.41	—2.35
Diethylbenzene	1.6	—	—
p-Xylene	1.7	0.43	—2.26
m-Xylene	1.8	0.47	—2.28
Ethylbenzene	1.8	—	—2.21
o-Xylene	1.9	—	—
Toluene	2.0	0.54	—2.02
Benzene	2.3	0.59	—1.74
Ethoxybenzene (phenetole)	[2.5]	(0.69)	—1.3
Methoxybenzene (anisole)	2.9	0.73	—1.05
Other compounds			
Carbon disulphide	[1.8]	—	—2.6
Hexamethylphosphoramide	[2.5]	0.87	—
Tributyl phosphate	[4.0]	0.65	—
1,4-Dioxan	[2.5]	0.55	—
Benzaldehyde	[3.5]	(0.92)	—0.44

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*The values of ID* obtained with the aid of correlation equations from the parameters of the π^* and lg k_i scales are given in square brackets.[66]

In comparing the different scales for the influence of diluents, it is essential to note that the ID* scale provides the most accurate correlation with lg P_0, because it has been derived directly from extraction data and already includes allowance for the differences between the molar volumes of the solvents. Furthermore, the other scales have been constructed for anhydrous solvents, while the ID* scale applies to diluents in equilibrium with the aqueous phase, i.e. under conditions closest to those which exist in real extraction systems. Moreover, the ID* scale is specially designed to describe extraction equilibria and applies to solvents which can be used as diluents; the other scales apply mainly to solvents miscible with water and to a lesser extent to hydrophobic solvents. Nevertheless, in those cases where the parameter ID* has not been determined for a particular solvent, approximate estimates may be made in terms of the π^* or lg k_i scales, whose parameters are also listed in Table 3, or on the basis of the approximate values of ID* calculated from them and indicated in Table 3 in square brackets.

The joint influence of the nature of the diluent and of the structure of the partitioned compound can be expressed by a single two-parameter equation[52] of the type

$$\lg P_0 = a + b\Sigma\pi_i + a\text{ID}^*, \qquad (12)$$

where a, b, and c are constant coefficients within the limits of a series of systems differing only in the nature of the diluent and the structure of the extractant. Thus the partition of trialkylamines is described by the equations lg $P_0 = -2.48 + 0.48n_C + 0.36\text{ID}^*$. A similar equation has been found[56] also for trialkyl phosphates.

In order to estimate the partition of trialkylammonium salts incorporating different anions in extraction by different diluents, we may employ the equation[69] lg $P_0 = a + 0.48n_C + 0.02\Delta G^*_{\text{hydr}} + 0.36\text{ID}^*$. The optimum length of the alkyl chain can also be selected on the basis of this equation for the practical employment of the amine salt as a function of the nature of this anion. It follows from the equation that, in order to maintain a sufficiently low solubility of the salt in the aqueous phase on passing from the anion NO_3^- to SO_4^{2-}

(ΔG^*_{hydr} then diminishes by ~200 kg g-ion^{-1}), it is necessary to increase the length of the alkyl chains in the amine salt by ~10 CH_2 groups (overall).

It follows from the data presented above that, in order to ensure the minimum contamination of the surrounding medium (the liquid waste or the solutions of the final products) by the dissolved extractant, one can increase the length of the alkyl chains or employ diluents with higher parameters ID*. Examples of the employment of extractants with lengthened alkyl chains to diminish their solubility in the aqueous phase have been described in a number of communications[70–73] dealing with studies of extractants with chains longer than in tributyl phosphate as possible substitutes for the latter in the extraction processing of the irradiated fuel from atomic power stations. A preliminary quantitative estimate of the expected decrease of the solubility was then obtained from an equation of type (11) and the parameters π. If it is nevertheless necessary to employ a relatively hydrophilic extractant, then the admixture of the latter can be washed out of the aqueous waste by fresh solvent; the effectiveness of the washing will then evidently increase with increase of ID* for the diluent. This makes it possible to select a suitable diluent from Table 2.

Since one can use in principle aqueous solutions containing hydrophilic organic additives in extraction schemes (sometimes a polar organic liquid immiscible with the non-polar organic solvent can also play the role of the aqueous phase), the results of studies of partition in such systems too are of interest. The applicability to systems of this kind of equations based on the principle of the linear free energy relations has been demonstrated[74] and for each new type of polar phase it is possible to set up a special scale of parameters of type characterising the contribution to lg P_0 of individual structural units of the substance passing to the non-polar phase. With decreased polarity of the polar phase, the quantities π diminish. We have found that in such systems the linear relations between lg P_0 and the ID* for the non-polar phase also hold, provided that the polar phase remains unchanged within the limits of the series.

The π_i, ID*, and ΔG^*_{hydr} scales have been created on the basis of a statistical treatment of large sets of extraction equilibrium data. For the treatment of such sets with the aid of a computer, the "OPAG" program has been developed.[53] It makes it possible to calculate not only the value of each parameter but also to obtain its statistical characteristics, which serve for the quantitative estimation of the accuracy of the prediction based on this parameter in each specific extraction system for a specified fiducial probability. Studies designed to expand and refine the scales indicated are being continued as interest grows in new diluents, extractants, and anions. The "OPAG" program makes it possible to introduce into the computer memory new additional data and to recalculate the entire set accumulated in the memory with a small consumption of computer time.

As mentioned above, the ID* scale (as well as the π^* scale) describes the influence of the nature of the diluent in systems where there is no specific solvation. For systems with specific solvation, whose influence on the extraction was first analysed in detail by the present author and his co-workers,[16,59] one may perhaps usefully employ an equation of type (11) including an additional term (increment) characterising the capacity of the diluent for the formation of donor or acceptor bonds. A scale based on such a series of increments has been developed in relation to solvatochromic effects.[95,96] A similar increment scale, reflecting the influence of specific solvation on physical partition, can probably be devised also on the basis of extraction data. The scale of ID parameters described below can be used for the combined allowance for the joint influence of non-specific and specific solvation in cases where the diluent exhibits electron-accepting properties.

Overall, the use of the tabulated values of ID*, π_i, and ΔG^*_{hydr} in combination with an equation of type (12) permits the reliable prediction of important characteristics of extractants associated with physical partition.

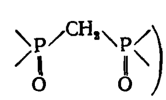
2. Equilibria In Extraction Processes Involving the Formation of Hydrophobic Compounds

Equilibrium systems of this type are most often used in technology and were therefore investigated in the first place (only recently has such attention been devoted to physical partition).

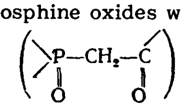
The Influence of the Structure of the Extractant

A preliminary estimation of the extraction capacity of a nucleophilic extractant (and hence of the constant K) is usually made on the basis of the available information about the capacity of its functional group for complex formation via a reaction of type (1). For example, if it is necessary to extract and separate palladium(II) from uranium(VI) in a nitric acid medium, then evidently one can use as the extractant a hydrophobic compound in which the functional group consists of the atom S, which is capable of forming coordinate bonds with the "soft" Pd^{2+} cations[97] but not with the "hard" UO_2^{2+} cations.[98]

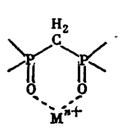
In selecting the functional group of the extractant, account must also be taken of the capacity of the cation extracted via reaction (1) for the formation of neutral complexes. Constants for extraction via the type (1) reactions are known[5,9–14] to increase with increase in the ability of the M^{n+} cations to coordinate the A^- anions. Therefore, for the extraction from nitrate solutions of, for example, plutonium(IV) or uranium(VI), whose cations form relatively readily neutral complexes with nitrate ions,[98] it is sufficient to employ monodentate extractants[99] incorporating one phosphoryl ($>P{=}O$) or sulphoxide ($>S{=}O$) functional group, such as tributyl phosphate or dioctyl sulphoxide. For extraction from nitric acid solution of tervalent lanthanide elements, which show a smaller tendency towards complex formation with NO_3^- ions, one has to employ bidentate extractants, for example, diphosphine oxide, with the functional group



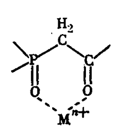
or carbamoylmethylphosphine oxides with the group[100–102]



which form more stable solvates with metal salts as a result of the formation of six-membered rings of type (I) or (II):

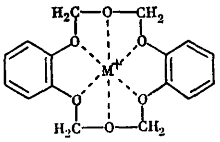


(I)



(II)

The extraction from nitric acid solutions of alkaline earth or alkali metals, which show an even smaller tendency to form complexes with NO_3^- ions, requires the use of polydentate extractants, incorporating more than two electron-donating groups or atoms, arranged in the form of a ring in order to render sterically feasible the simultaneous formation of a large number of bonds with the cation extracted. "Crown" ethers, for example dibenzylcrown-6 ether (III), belong to extractants of this type:[103,104]



(III)

The preliminary selection of acid extractants is made taking into account the fact that constants for extraction via reactions of type (3) increase with increase of the dissociation constants of the extractant. After the type of functional groups or group of the extractant has been chosen, the structures of the substituents attached to these groups are optimised[105] in order to achieve the best extraction and selectivity and also the greatest compatibility of the extractant and the compounds extracted with the diluent.[16] The most suitable diluent, into which the extractant and solvate will be effectively extracted as a result of physical partition, is also chosen.

As stated above, not only qualitative but also quantitative prediction of the influence of various factors on K is frequently needed at the optimisation stage. In both cases the prediction can be based on the use of the principles of linear free energy relations (LFE).

Starting from 1964–1965, the possibility of predicting the equilibrium constants of extraction processes of type (1) with the aid of parameters familiar from organic chemistry, namely the Hammett (σ), Kabachnik (σ_ϕ), Taft (σ^*), etc. constants,[17,74,75] for the substituents attached to the functional group of the extractant and included in equations of the type $\lg K = a + b\Sigma\sigma$ based on the LFE principle has been established for reactions of types (1)–(3). However, such equations are inapplicable to organic series of extractants where the steric factors governing the influence of substituents vary insignificantly. The need to take account also of the steric factors by employing equations of the type

$$\lg K = a + b\sum\sigma^* + c\sum E_S^* , \tag{13}$$

where σ^* are the induction constants (Taft constants) and E_S^* the steric parameters of the substituents at the functional groups of the extractants, has been demonstrated for the general case.[19,76] In order to describe the large sets of extraction data, it was necessary to develop the E_S^* scale, differing somewhat from the familiar Taft (E_S) scale.[17,74,75] The equation found[19,76] for the extraction of nitric acid by the nitrates of 16 tertiary amines of different structure dissolved in xylene, namely $\lg K_{HNO_3} = -0.20 - 0.28\Sigma\sigma^* + 0.79\Sigma E_S^*$, may serve as an example of the exact description of a large set of values of K.

Similar analysis of the factors influencing the sensitivity coefficients b and c in equations of type (13) using different types of extractants and also a detailed compilation of the correlation equations of type (13) for different systems may be found in a review.[17]

The equation without the term including the constants E_S^* may be applicable to phosphoryl-containing extractants, provided that the Kabachnik parameters σ_ϕ are used. The quantitative relation between the structure and extracting power of organoelemental extractants has been analysed recently.[78]

The approach to the quantitative description of the influence of the structure of extractants and of the nature of the compound extracted developed in recent years is also of interest. It is based on the use of two-parameter equations incorporating terms which take into account the ability of the components to form both polar and covalent bonds. The principles of this approach have been described in detail.[77]

The Influence of the Nature of the Diluent

It has been established[24] that, for the series of systems where extraction is determined by type (1) reactions, the LFE principle holds when the nature of the diluents is altered. An ID scale[12] (Table 4), reflecting[55,57] the joint influence of the non-specific and specific solvation of the nucleophilic functional groups of the extractant by diluent molecules, has been developed on the basis of the statistical treatment of a large set of extraction data. It has also been shown that equations of the type

$$\lg K = a + b\text{ID}. \tag{14}$$

hold for a large series of extraction systems in which only the nature of the diluents is varied.

Table 4. The parameters ID of the diluents.[12]

Diluent	ID	Diluent	ID
n-Octane	(0.20)	1,2-Dichloroethane	−0.16
Cyclohexane	0.50	Nitrobenzene	(−0.03)
Butylbenzene	(0.23)	Chloroform	−1.52
p-Xylene	0.10	Cyclohexane + benzene (1 : 1)	0.20
o-Xylene	0.10	*p*-$(C_2H_5)_2C_6H_4$	0.12
Benzene	0.0	$(C_2H_5)_3C_6H_3$	(−0.26)
Chlorobenzene	−0.15	*o*-(iso-$C_3H_7)_2C_6H_4$	0.35
Bromobenzene	−0.30	Toluene	0.03
Anisole	(0.18)	85% Decane + 15% chloroform	−1.12
Bromobenzene + CCl_4 (1 : 1)	−0.50	90% Tetradecane + 10% chloroform	−0.75
CCl_4	−0.60	85% Tetradecane + 15% chloroform	−1.12
Bromocyclohexane	(−0.45)	99% Cyclohexane + 1% octanol	(0.53)
95% Benzene + 5% decanol	(−0.20)	98% Cyclohexane + 2% octanol	(0.53)
Cyclohexanone	(0.30)	97% Cyclohexane + 3% octanol	(0.43)
80% Octane + 20% chloroform	−1.40	96% Cyclohexane + 4% octanol	(0.38)
80% Decane + 20% chloroform	−1.47	94% Cyclohexane + 6% octanol	(0.30)
80% Decane + 20% octanol	(−2.20)	90% Cyclohexane + 10% octanol	(0.23)
95% Benzene + 5% chloroform	−0.40	96% n-Hexane + 4% octanol	(0.12)
90% Benzene + 10% chloroform	−0.65	95% Benzene + 5% n-decane	(−0.20)
85% Benzene + 15% chloroform	−0.80		
80% Benzene + 20% chloroform	−1.20		
90% Octane + 10% chloroform	−0.77		
85% Octane + 15% chloroform	−1.23		
90% Decane + 10% chloroform	−0.80		

Examples of linear relations of this type for the extraction of HNO_3 by ammonium nitrates and the extraction of plutonium(IV) nitrates and HNO_3 by neutral phosphoryl-containing extractants have been published.[50,106]

In those cases where the extraction proceeds via reactions (2) and (3), leading to appreciable changes in the polarity of the components of the organic phase, the influence of the diluent is determined to a large extent by the non-specific solvation of the extractant molecules by the diluent. For these systems, the influence of the diluent is determined by an equation of type (14), but, instead of the parameters ID, it is necessary to employ in this instance the parameters ID*, i.e. those which describe the corresponding effects in physical partition.

Detailed compilations of the dependence of $\lg K$ on ID and ID* have been published[17] and an analysis separating the regions in which these parameters are applicable has been carried out.[55,57] The applicability of the parameters ID* has been recently confirmed.[67,72]

The Joint Influence of the Structure of the Extractant and of the Nature of the Diluent

It was found for the first time in 1970[12] that electrophilic diluents, solvating specifically the nucleophilic group of the extractant, have a levelling effect on the extracting power of nucleophilic extractants of different structures. This effect can be expressed quantitatively by a linear relation, which makes it possible to describe[80,107] the sets of data for systems in which the structure of the extractant and the nature of the diluent are varied simultaneously by equations with a "cross" term of the type

$$\lg K = a + b\mathrm{ID} + \rho\Sigma\sigma + d\mathrm{ID}\Sigma\sigma. \tag{15}$$

For example, the set of constants for the extraction of plutonium(IV) nitrate by neutral organophosphorus compounds (NOPC) is described[106,107] with a high accuracy by the equation $\lg K_{\mathrm{Pu}} = -0.18 + 3.03\Sigma\sigma_{\phi} + 0.30\ \mathrm{ID} - 0.33\ \mathrm{ID}\Sigma\sigma_{\phi}$. Equations of a similar type also describe the large set of constants for the extraction of nitric acid and uranyl nitrate by NOPC, sulphoxides, and arsine oxides of different structure in different diluents[80] and also the extraction of HNO_3 by substituted ammonium salts.[19,50]

The use of Eqns.(13)–(15) makes it possible to predict reliably the extracting power of extractants of different structure in various diluents using tabulated values of σ_{ϕ}, σ^*, E_S^*, and ID, which is done for the selection of extraction systems with optimum composition as regards extractant and diluent.[70,82–84] Such prediction has been adequately achieved for a series with a constant functional group of the extractant. When the functional groups are varied, the changes in the sensitivity coefficients in equations of types (13)–(15) have so far been understood only qualitatively. The task of the future development of a theory is the development of methods for the quantitative estimation of the influence of the replacement of the functional groups of the extractants themselves on the coefficients of Eqns.(13)–(15).

The Influence of the Nature of the Anions and Cations Participating in the Extraction

It has been established that the extraction by amines of anions in the form of acids via the neutralisation reaction[85] or in the form of ionic associated species when quaternary ammonium salts or complexes of metal salts of crown ethers are extracted depends on the parameters of the hydration of anions $\Delta G^*_{\mathrm{hydr}}$ in accordance with the equation $\lg K = a + \Delta G^*_{\mathrm{hydr}}$. The quantities $\Delta G^*_{\mathrm{hydr}}$ for ~80 different anions have been evaluated by the appropriate treatment of a large set of extraction data[27,53] (Table 2). Using the parameters in Table 2, it is possible to predict the influence of the changes in the nature of the anion on the extraction constants.

When the anions A^- and X^- are exchanged, i.e. in extraction via reaction (5), the extraction constant can be expressed by the equation

$$\lg K = \varkappa(\Delta G^*_{\mathrm{A}} - \Delta G^*_{\mathrm{X}}) \tag{16}$$

The correlation equations of type (16) have been compiled and the factors influencing the selectivity coefficient κ have been analysed.[52,53] Numerous examples of the use of equations of type (16) have been published.[86–90]

In order to estimate the influence of the nature of the anionic ligands on the extraction of salts of "hard" cations and acids via addition reactions of type (1), it has been suggested[92] that the Edwards nucleophilicity parameters H be used in combination with equations of the type $\lg K = a + bH$, where a and b are sensitivity coefficients which are constant within the limits of a series of extraction systems differing only in the nature of the anionic ligands. Examples of such relations for the extraction of acids and uranium(VI) salts (from solutions in identical acids) by substituted ammonium salts and also the parameters H have been published in reviews.[14,17]

It has also been found that the LFE principle holds for the extraction of "hard" cations via type (1) reactions by nucleophilic extractants[93] and the possibility of predicting in a number of instances the extraction constants with the aid of an equation of the type $\lg K = a + b\mathrm{IE}$, where IE are empirical parameters (the "influence of the element") characterising the "hard" cations, has been demonstrated. This approach agrees with the ideas developed independently in a study[94] where it was suggested that the parameters of the empirical f_{M} scale be used as parameters characterising the cations. The possibility of this application of the parameters E_{M}, calculated by Petrukhin and Borshch,[108] characterising "soft" cations has been recently demonstrated for the extraction of such cations.

The Joint Influence of the Nature of the Anions and Diluents

In the absence of specific solvation, the values of lg K for the extraction of acids via neutralisation reactions vary linearly with the parameters ID^*. For systems of this type, the slope of the plot of lg K against $\Delta G^*_{\mathrm{hydr}}$ is almost independent of ID^*, which makes it possible to describe large sets of data with the aid of two-parameter linear equations without cross terms. For example, the equation

$$\lg K_{\mathrm{HA}} = 16.51 + 1.196\mathrm{ID}^* + 0.181\Delta G^*_{\mathrm{hydr}}$$

is valid[90] for the extraction of acids incorporating different anions by solutions of trioctylamine (TOA) in different diluents. Equations of this type are valid in the absence of appreciable specific solvation (ID $\geqq -0.6$). When specifically solvating diluents are used, the coefficient of $\Delta G^*_{\mathrm{hydr}}$ may decrease on passing to the most electrophilic diluents—alcohols, chloroform, etc.[52]

The Influence of the Quantitative Composition of the Aqueous Phase

Such influence can be described with the aid of equations of the type $\lg D = a + b\mathrm{IAP}$, where a and b are coefficients which remain constant within the limits of a series of systems differing only in the composition indicated and IAP is a parameter characterising the composition of the aqueous phase.[17] Examples of the employment of the parameters IAP for the calculation of partition coefficients have been published.[109–115]

All the equations examined above, which make it possible not only to predict the extraction constants for different systems but also to describe with the aid of a small number of equations large sets of data, which is only important in connection with the continuing increase in the volume of information on extraction equilibria.

Equilibrium Partition in Extraction by Mixtures of Extractants

In order to enhance the extraction properties, synergistic mixtures are sometimes used. Mixtures of acids and neutral extractants are commonest. The increased extracting power of such mixtures is explained by the formation of adducts of the neutral extractants with the hydrophobic metal salts formed by the acid extractant. Many investigators still continue to carry out laborious experiments in order to determine the influence of the nature of the diluent on extraction constants by such mixtures disregarding the fact that simple relations have been established whereby one can predict the positions of such equilibria without carrying out experiments or with a minimal number of experiments. It has been established that lg K usually decreases linearly with increase in ID* for the diluent, falling more steeply than for the individual acid extractants:[116] the fall is determined by the sum of the effect of the diluent on lg K for the acid extractant and lg Q (the formation constant of the adduct), which also decreases linearly with increased ID*. As for acid extractants, the slope of the dependence of lg K on ID* diminishes as the extractant becomes more hydrophilic, because the contribution of the changes in P_0 increases in this case.

A change in the nature of the neutral extractant forming part of the composition of the mixture influences the synergism as well as the extracting power of the extractant itself, i.e. this influence can be predicted with the aid of the parameters σ_ϕ, σ^*, and E^*_S.

3. The Selectivity in the Separation by Extraction of Elements Having Similar Properties

The survey of a large number of data on the practical application of extraction shows that the factors influencing the separation of elements with relatively similar properties are frequently not the same as the factors influencing the thorough elimination of poorly extractable impurities from readily extractable elements. For this reason, in these two cases it is desirable to carry out separately the analysis of the factors influencing the selectivity of the extraction.

The problem of the separation of elements with similar properties preceded historically a second problem, which might have been solved by a simple repetition of the extraction cycles and has arisen solely because of the requirement for economy.

On the other hand, the separation of elements with relatively similar properties has engaged the attention of chemists over several decades.

As noted above, the first step in choosing a selective system involves the choice of the functional group of the extractant and the composition of the aqueous phase on the basis of the available information about the complex formation. The next step is to optimise the structure of the extractant and the nature of the diluent in order to increase the separation factor, which is especially important when the elements to be separated have similar properties. For this purpose, the extraction equilibria are analysed with the aid of the Law of Mass Action (LMA) and LFE.

It follows from the LMA that the partition coefficient of the extracted element is proportional to the concentration of the extractant raised to a power equal to the solvation number. For this reason, as the concentration of the extractant rises, the value of D for the element forming the higher solvate increases faster than that for the element which forms the lower solvate. Therefore, if the first element is extracted no less effectively than the second, it is evident that the separation factor will increase with increasing extractant concentration, while in the opposite case it will fall. For example, plutonium(IV) is extracted in the form of a disolvate by an amine in nitrate systems, while uranium(VI) is extracted as the monosolvate, plutonium(IV) being extracted more effectively than uranium(VI). The separation factor Pu(IV)/U(VI) in this system can therefore be appreciably improved by increasing the extractant concentration. This is also characteristic of the extraction of plutonium(IV) and uranium(VI) by acid extractants of the type of thenoyltrifluoroacetone with which plutinium(IV) reacts to form 1:4 compounds, while uranium(VI) forms 1:2 compounds.

Next, for the same solvation numbers and for approximately equal capacities for being extracted, the separation factor can be increased by saturating the extractant with the main element present in excess. The concentration of the free extractant then diminishes and the degree of extraction of the impurity element diminishes correspondingly according to the LMA. If the excess of the main element is small, it can be generated artificially by devising an appropriate arrangement of flows ensuring the return of part of this element to the cycle after purification. The effectiveness of this procedure, referred to as the reflux process, has been demonstrated[117,119] etc. The data presented demonstrate the fruitfulness of the application of the LMA to the selection of the optimum conditions in extraction purification. The use of the LMA for the analysis of extraction conditions was initiated in our country by Fomin[9] who, starting in 1955, has used and vigorously advocated this procedure which has been adopted by many investigators.

The employment of equations based on the LFE principle is also very fruitful. Thus, when the structure of the extractant is altered, it is necessary to analyse the influence of various factors in terms of the expression

$$\beta_{1,2} = a + b\Sigma\sigma^* + c\Sigma E^*_S,$$

where $\beta_{1,2}$ is the separation factor for the elements (1) and (2). This expression can be obtained from Eqn.(13) bearing in mind that lg $\beta_{1,2}$ = lg D_1−lg D_2. Analysis with the aid of this expression, for example, of conditions governing the separation of the tervalent actinides, which have similar properties, in extraction by substituted ammonium nitrate has demonstrated[120] a relatively high and positive value of the coefficient of $\Sigma\sigma^*$ and a low value of the coefficient of ΣE^*_S. This led to the conclusion[120] that extractants with (as far as possible) a positive value of $\Sigma\sigma^*$ should be used and at the same time one should have an amine with a high value of $|\Sigma E^*_S|$ in order to attain a fairly high value of D. Indeed, among tertiary amines, methyldioctylamine is more selective than trioctylamine, whereas for trialkylamines with a longer chain $\Sigma\sigma^* \cong$ const. while ΣE^*_S diminishes and the values of $\beta_{1,2}$ therefore differ little.

In certain systems where only one structural factor is varied, an increase in the partition coefficient is observed following an increase of steric hindrance. For example, the separation factor Pu(IV)/Th(IV) increases on extraction with trialkylamines[50] in accordance with the equation

$$\lg \beta = a - b\Sigma E^*_S.$$

However, this is true for identical solvation numbers. For different solvation numbers, analysis of the data on the basis of the LFE principle and the finding that for each compound the slope of the dependence of lg β on the parameters σ^* and E^*_S increases with increasing solvation number enabled us in 1978 to formulate the following rules[17] which determine the influence of the structure of the extractant, the nature of the diluent, and the nature of the anionic ligand on the selectivity of the extraction process.

1. For a series of extraction systems differing solely in the nature of the metals extracted but characterised by the same solvation numbers, the same composition of the complex extracted, and the same type of nucleophilic extractant, the selectivity in the extraction of these metals increases following the changes in the inductive and steric effects of the substituent† associated with the increase in $\Sigma\sigma^*$ or the decrease in ΣE^*_S.

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†This rule has been formulated earlier also in other studies.[121,122]

2. If the complexes of two elements extracted in the given extraction system have different solvation numbers, then the change in the nature of the substituent leading to an overall decrease of the extracting power (increase of $\Sigma\sigma^*$, decrease of ΣE_S^*) entails a fall in the selectivity of the extraction if the element whose complex has the smallest solvation number differs also by having a smaller capacity for being extracted and increases if the element is extracted more effectively than the element whose complex has the higher solvation number.

3. For systems in which the influence of the diluent can be expressed by the dependence on ID for identical solvation numbers of the two elements extracted, the selectivity of the extraction by the given nucleophilic extractant increases with decrease in the parameter ID for the diluent, i.e. with increase in the ability of the diluent to solvate the nucleophilic functional group of the extractant.

4. If the compounds of the salts of the two metals are characterised by different solvation numbers, then the selectivity increases with increase in ID, provided that the complex with the higher solvation number corresponds to the more effectively extracted element.

5. In cation exchange reactions, the increase in ID^* hinders the reactions involving the conversion of acids into metal salts and reduces the selectivity of the extraction of the latter (for equal solvation numbers).

6. In an anion exchange reaction, the increase in ID^* favours to a greater extent the occurrence of reactions leading to the formation of more polar compounds in the organic phase, i.e. the increase of ID^* tends to increase the selectivity of the extraction of the anions of the stronger monobasic acids from a medium comprising weaker acids and of the extraction of singly charged ions from a medium comprising doubly charged and multicharged anions.

7. The selectivity of the extraction for a pair of elements where the cation of one element is "hard" while the other is a "soft" Lewis acid, can be increased by going over to anions with a higher value of H in those cases where the "hard" element is extracted more effectively or by going over to anions with a low H where the "soft" element is more readily extracted.

When the two anions to be separated are extracted by the anion exchange mechanism, the selectivity is determined by the anion exchange extraction constant for the given pair of anions, which is determined by Eqn.(16). It has been established that the coefficient κ in Eqn.(16) depends on the nature of the extractant cation and in a non-specifically solvating diluent is 0.235 for quaternary ammonium bases; for tertiary amines, it amounts to 0.16–0.18. The selectivity of the extraction of anions falls sharply when a specifically solvating electrophilic diluent is employed, because, as mentioned above, when highly solvating diluents such as octyl alcohol are employed, the dependence of lg K or ΔG^*_{hydr} is weak and the selectivity of the separation of singly charged anions is correspondingly low.[52]

Using Eqn.(16), the ΔG^*_{hydr} scale, which is known for ~80 anions, and the coefficients κ determined for ~80 series of systems, it is possible to predict the selectivity in the extraction of anions for different combinations of 80 anions in 80 series, i.e. for ~7.5×10^5 different extraction systems. It has been shown[27,53] that, with the aid of the "OPAG" program, it is possible to determine not only the 7.5×10^5 anion exchange extraction constants but also the accuracy of each prediction for a specified fiducial probability. This result[53] is apparently the most striking example of the effectiveness of the application of the LFE principle to the prediction of extraction constants.

4. Properties Associated with the Interaction at the Interface and Determining the Extensive Separation of Elements Having Different Properties

The principles governing the prediction of the extracting power examined above have proved applicable to the prediction of the surface-active properties of extractants and diluents at the interface[123–127] and to the estimation of the optimum conditions governing the extensive separation of elements with different properties.

The interfacial tension is a property on which depends the rate of separation of two phase systems into different layers in extraction apparatus, which determines the productivity of the extraction equipment. It has been established that the interfacial tension γ at the water–diluent interface decreases with increase in the parameter ID^* for the diluent. For solutions of nucleophilic extractants, γ increases with increase in the above parameter.[126,127] All the nucleophilic extractants are surfactants. The energy of their adsorption at the interface W, which determines the interfacial tension γ, varies linearly under these conditions with the sum of the Kabachnik parameters for the substituents at the nucleophilic centre, for example at the P=O group.[125] If the extractant is a salt of an amine or a quaternary ammonium base, W varies linearly with $\Sigma\sigma^*$ and ΣE_S^* for the substituent and, when the nature of the anion is altered, then W varies linearly with the parameter ΔG^*_{hydr} for the anion of the substituted ammonium salt.[128]

The above findings can be understood if account is taken of the fact that the surface activity of the nucleophilic extractant, expressed by its adsorption at the interface, is determined by the same factors as its extracting power, i.e. the basicity of its functional group. Any factors which reduce this basicity (the replacement of the substituents at the functional group, its solvation by the diluent, and the change in the nature of the anion of the substituted ammonium salt, which is itself a functional group) reduce also the surface activity. The binding of the nucleophilic functional group on formation of the solvate via a type (1) reaction has a particularly marked influence. For example, it has been shown[129–131] that the formation of the disolvates $UO_2(NO_3)_2 \cdot (TBP)_2$, $Th(NO_3)_4(TBP)_2$, and $Pu(NO_3)_4(TBP)_2$ in the extraction of the nitrates of these elements by tributyl phosphate (TBP) very greatly reduces the interfacial activity in the corresponding extraction system.

These findings, combined with the parameters ID^*, σ, E_S^*, and ΔG^*_{hydr} are also used to optimise the structure of the extractant and the nature of the diluent in order to take into account the changes in the surface properties occurring under these conditions.[69,132] The equations based on the LFE principle for the prediction of the interfacial activity and the factors governing the separation of extraction emulsions into layers have been surveyed.[123] The possibility of predicting the interfacial tension confirms the effectiveness of the LFE concept as a means whereby the properties of extraction systems can be predicted.

The application of external electrical and magnetic fields influences markedly the properties of the interface. These phenomena, which may be employed in the extraction technology of the future, are at present in the initial stage of their investigation.[133,134]

If two elements have markedly different partition coefficients then, in principle, having ensured a sufficient number of stages in the washing of the extract under conditions where the extraction coefficient of the valuable element is greater than unity and that of the impurity element is much less than unity, one can expect the attainment of separation (purification) factors as large as may be desired. In reality, the purification coefficient attainable in practice is usually limited to 10^5–10^6 even when the impurity element virtually is unextractable under the selected condition. The explanation is that, after the separation of the main bulk of the impurity, a small proportion of the latter remaining in the extract (10^{-4}–10^{-5}) is retained by it and cannot be washed out.

This may be caused by the mechanical entrainment of this part of the impurity in the form of a microemulsion of the aqueous phase in the organic phase, in the form sorbed on some kind of entrained solid microparticles, in the form of a complex with a microimpurity in the extractant capable of extracting the impurity element, and in the form of a complex with some kind of anion present as a microimpurity in the aqueous phase and forming an extractable compound with the impurity element.

The probability of the formation of microemulsions as well as the entrainment of solid microparticles increases with decrease in the interfacial tension, i.e. with increase in the surface activity of the component of the extraction system at the interface. For this reason, an increased degree of purification is promoted by any measures which reduce the interfacial surface activity. We shall consider this postulate in relation to extraction by trialkyl phosphates. When account is taken of the characteristics of the influence of the structure of the extractant on the interfacial activity, mentioned in Section I, the parameters σ_ϕ of the substituents (Table 3) permit the conclusion that an increase in the length of the alkyl chain of trialkyl phosphates (TAP) entails an increase in the interfacial tension. This factor, together with those examined above (Section II, 1), must be taken into account in selecting the optimum chain length. Evidently the increase in the length of the alkyl chain should improve the conditions for extensive purification at the extractant stage. At the same time, an unduly great increase in the length of the alkyl chains of the TAP can give rise to difficulties in other operations in technological schemes, for example in the washing out of the products of the hydrolysis of the TAP by alkaline solutions.[135] The optimum length of the alkyl chain of the TAP is chosen[69] in such a way that the best extraction conditions are ensured simultaneously with sufficiently effective remaining operations of the extraction cycle.

It is useful to employ a diluent with a high ID^*, other conditions being equal, because it has been shown[126,127] that this tends to reduce the interfacial activity.

Systematic investigation of the influence of various factors on the interfacial activity has shown[129–131] that the binding of the extractant in a solvate complex with a metal salt reduces its surface activity to that of the pure diluent and the overall surface activity is determined by the presence of the free extractant. From this, it follows that the saturation of the extractant by the salt of the metal extracted is essential not only for the suppression of the extraction of impurity elements with similar properties (see above) but also for the attainment of a high degree of elimination of mechanically entrained non-extractable impurities (in the form of microemulsions or solid particles). It is noteworthy that the removal of mechanically entrained impurities—elements incapable of forming stable complexes—can increase the degree of purification not only in the extraction stage but also in the course of subsequent operations, provided that the latter are based on complex formation, extraction, or ion-exchange sorption of the impurity element.

In view of the strong influence of the formation of an emulsion on purification during extraction, increasing attention is being devoted to this problem. Interesting results have been obtained by Moyer and McDowell[136] and Yagodin and Tarasov.[137] Ideas concerning the factors influencing emulsification, developed initially for petrochemical processes and the protection of the environment and surveyed in a number of communications,[138–140] are fully applicable to extraction processes.

The type of emulsion has a marked influence on the emulsification and on the separation of the emulsion into layers. The formation of a microemulsion is more probable in the continuous phase and is less likely in the disperse phase. On the other hand, if the microparticles entrained by the organic phase or concentrated at the interface are more effectively wetted by the aqueous solution, then they are more effectively separated if the organic phase is the continuous phase in the extraction process. Useful data about the factors influencing the rate of separation of the phases into layers as a function of the type of emulsion, the hydrophilic properties of the solid particles present in the system, and the length and the degree of branching of the alkyl chains of the extractant have been published.[136]

Microimpurities in the extractant, which, as stated above, can be the second cause limiting a high degree of purification, may be formed following the slight decomposition of the extractant in the cycle and are usually removed in one of the operations of the cycle as a result of dissolution in the aqueous phase. In order to assess the possibility of removing the microimpurity, one can employ equations relating P_0 to the structure of these compounds and the nature of the diluent. For example, it is possible to assess in this way the possibility of the "automatic" removal in the given cycle of admixtures, harmful to the purification process, of acid alkyl phosphates formed as a result of the hydrolysis of trialkyl phosphates or salts of primary amines which are produced on decomposition of extractants of the type of trialkylamines. Evidently the chain length of the nucleophilic extractants should be optimal, i.e. such that its solubility in water is sufficiently low and the solubility of the harmful decomposition product sufficiently high for removal from the organic phase during the operation of the extraction cycle.

These considerations are used in selecting the optimum structure of the extractant, the nature of the diluent, and the extraction conditions in order to obtain especially high purification coefficients in extraction cycles. As the technology develops, the requirements for the preparation of ultrapure materials will probably increase and an increase in the separation factors to 10^9 and above will be needed. For this reason, further search for methods whereby the degree of separation of elements with different properties can be increased for a minimal number of operations should remain of crucial importance in the future.

III. OPTIMISATION OF THE STRUCTURE OF EXTRACTION SCHEMES

1. Schemes With a Countercurrent (Structure, Modelling, and Regulation)

Schemes with a multistage countercurrent of aqueous and organic phases satisfy most completely the requirements for a high degree of extraction. Modern technological schemes are frequently characterised by a complex structure of the flows, organised in such a way that a high degree of saturation of the extractant by the target element can be achieved when necessary (as mentioned above, this is essential for the improvement of purification) or the part of the valuable component washed out together with the impurities during the washing of the extractant can be returned to the system for re-extraction.

The boundary conditions governing the operation of any scheme consist in the requirement that the concentration of the metal extracted in the organic phase should not exceed the capacity of the extractant and that the concentration in the discarded solution should not exceed the specified losses. Furthermore, as a rule the process should be stationary, i.e. there should be no changes in the accumulation of the element in any part of the countercurrent apparatus as a function of time. To test that these conditions are maintained and that the optimum current scheme can be selected, it is necessary to calculate the distribution of all the components among the different stages of the scheme in the steady-state regime; it is frequently essential to estimate the redistribution of the components among the stages for particular deviations from the nominal regime (in order to develop control and regulation systems). In certain instances, it is preferable to employ semicontinuous schemes in which the valuable component is deliberately accumulated (as a function of time) in a particular stage of the countercurrent apparatus.[141] It is then also necessary to estimate the distribution of the element or compound extracted among the stages taking into account in addition also the process time.

All the calculations indicated are carried out with the iterative formulation of the material balance equations at each stage taking into account the partition coefficients among the stages at the concentrations of the components yielded by the calculation. The use of mathematical modelling for calculations on countercurrent extraction processes was initiated in the USSR approximately 25 years ago by Fomin and Rozen and co-workers[142,143] and at the present time this field has been greatly improved as a result of the efforts of a large number of investigators—both chemists and mathematicians.[144–151] When the number of stages is large, the calculations are laborious, but nowadays they can be successfully performed with the aid of computers. For example, calculation on a computer of type EC-1055 sometimes takes several tens of minutes, a period which is acceptable for the calculation of particular regimes in the planning or development of the process but is much too long if the calculation is performed in order to control the process. For this reason, the construction of high-speed computational schemes constitutes an urgent task for the further development of models. An example of the creation of a high-speed algorithm for calculations on countercurrent extraction is provided by the study of Rozen and Zel'venskii.[152]

The first models included partition data obtained on the basis of the LMA; they require the knowledge of a large number of constants (the extraction constants and the stability constants of all the complexes in the aqueous phase) and the activity coefficients of all the compounds present in the system. Subsequently much attention was devoted to the creation of purely empirical models with the smallest number of constants requiring determination. For the distribution of microconcentrations, the model consists of the IAP function (see above) to which the partition coefficients D are linked (on the basis of the LFE principle) by a simple linear relation. A characteristic feature of the IAP function is that it is the same for a series of elements with similar properties, for example, for the extraction of UO_2^{2+}, WO_2^{2+}, MoO_2^{2+}, PuO_2^{2+}, and NpO_2^{2+} or for U^{4+}, Pu^{4+}, Np^{4+}, Th^{4+}, and Hf^{4+}. In all complex cases, for example, in the case of the simultaneous extraction of several elements at macroconcentrations, one can employ purely empirical formulae fitted to the dependence of D on the contents of different components in the solutions. These relations frequently proved to be simpler and more accurate than those based on the LMA. The countercurrent distribution models, constructed using these formulae, made it possible to devise algorithms and programs for computer calculations which are very fast to execute.[1]

In systems for which there are large sets of experimental data, the "formally rigorous" descriptions of the equilibrium, having the form of the LMA but including a number of assumptions based on empirical relations, are also used. Such successfully realised models include those taking into account the surface density of the hydration of cations, a concept developed in a number of studies,[40,153,154] or including the extraction "constants" expressed by an empirically fitted function of the composition of the aqueous phase.[43,44]

The use of mathematical models for apparatus with discrete stages makes it possible to determine the structure of the control system on the basis of the measurement of the location of the front of the extracted element in the countercurrent apparatus choosing for this point the stages between which the concentration gradient is greatest.

The use of mathematical models for apparatus with discrete stages permits the calculation of the concentration at each stage under different conditions,[154,155] including those where the normal process conditions are infringed, and thus permits the estimation of the results of possible infringements.

For column (non-discrete) countercurrent extractors, the creation of a mathematical model for the distribution along the height of the apparatus is more complicated, because such distribution is much more subject to the influence of both kinetic and hydrodynamic factors, such as the possible changes in the "arrest" of the disperse phase, when the flow rate of the solutions and the supply of external energy for the dispersion of the phases are altered. The development of models for such apparatus is an important task, because column extractors, together with extractors of the mixing-settling type, are widely used in practice.[1,156]

An important task in the field of the modelling of countercurrent extraction is as far as possible a more accurate quantitative description of the dependence of the distribution of all the components of the system of interest to technology on its composition. This requires further study and description with the aid of suitable empirical formulae of the experimental data obtained for the distribution of different elements which are of interest and which are re-extracted as the technology develops. The most detailed studies on these lines have been carried out for the description of the distribution of actinide elements and elements which are fission products.

2. Periodic Extraction, Membrane Extraction, and Extraction Chromatography

Countercurrent extraction is not the only possible extraction scheme. In certain cases it may prove useful to employ also other schemes for extraction processes. If it is necessary to employ an extractant with a comparatively high solubility in the aqueous phase or one which is particularly scarce, whose losses must be reduced to a minimum, and also in the case where it is necessary to reduce to a minimum the access of the extractant to the aqueous solution (for example, in extraction from biological liquids), one can employ membrane extraction.[157] In this variant, the extractant is separated from the aqueous solution by a thin semipermeable partition. To accelerate the process, whose characteristic features hardly differ as regards partition from those of the usual extraction, an electrical potential difference is applied to the system. The development of the theoretical principles of this process is of great interest.

A novel method, called "emulsion membrane extraction", began to be developed during the last decade.[158,159] It makes it possible to combine extraction with re-extraction. The method consists in incorporating initially the solution to be re-extracted in the extractant phase in the form of a stabilised emulsion of the water/oil type. The resulting mass is then dispersed in the aqueous phase to form an emulsion comprising drops of the extractant with smaller drops of the re-extractant incorporated in them. As a result of this, extraction and re-extraction take place simultaneously, which ensures a high extraction coefficient per extraction stage. The possibilities of this method are still being investigated[159] and will probably be limited by the requirement that sufficiently stable emulsions of the re-extractant in the extractant be obtained. The choice of the appropriate emulsifying agent is apparently the main problem. The growing interest in emulsion membrane extraction is indicated by the appreciable growth of the number of publications on this question during recent years.[160-163]

Extraction chromatography, a method in which the extractant is deposited on a solid carrier, occupies the boundary between extraction and sorption.[164] Here the characteristics of the partition are the same as in extraction. The factors influencing the equilibrium partition quoted above are applicable to this process. As regards kinetics and apparatus, the method is closer to sorption processes.

3. The Choice of the Composition of the Aqueous and Organic Phases for a Waste Free Technology

As noted above, a characteristic feature of extraction methods is the almost complete absence of the consumption of the reagent and hence of salt waste. For this purpose, one selects extractants which possess a sufficient but moderate extraction power so that re-extraction can be carried out with water without using complex-forming agents and other reagents. The extracting power must be such that there is no need to employ a salting-out agent in the extraction stage. For example, very weak extractants—carboxylic acid esters—require the addition of salting-out agents (nitrate salts) in order to extract uranyl nitrate, although the re-extraction is carried out with water.[165] On the other hand, trioctylphosphine oxide extracts uranyl nitrate effectively from dilute nitrate acid but the re-extraction with water is impossible; it is necessary to employ a solution of complex-forming agents.[166] The optimum extractant is in this case TBP—the extraction is from a 2–3 M HNO_3 solution and the re-extraction is carried out with water. There are no reagents other than HNO_3, which can be concentrated (distilled) from the refined product and returned to the cycle.

Similar approaches are necessary also in the extraction of other elements: this is achieved by selecting extractants of appropriate strengths. Thus the introduction of salting-out agents is necessary to extract americium or the lanthanides from nitrate solutions by tributyl phosphate. However, stronger bidentate extractants[101-105] or phosphoric triamides[167] extract these elements from 2–3 M HNO_3 and permit re-extraction into water.

The extraction of elements such as caesium is still more difficult. As mentioned above, a solution involves the employment of polydentate extractants in which the simultaneous operation of all the functional groups is ensured by the cyclic structure of the extractant skeleton (crown). These extractants are able to extract caesium and strontium from nitric acid solutions without the use of salting-out agents in re-extraction with water.[168,169]

In the specific selection of the optimum structure of the bidentate extractant and of the diluent, one can be guided by the rules described above (Section II).

A promising method for the removal of reagents involves the use of electrochemical re-extraction methods, which are at present in the stage of intense research, where the element is converted into a non-extractable valence state by passing an electric current through the solution.[1] The use (in order to change the valence of the extractable elements or the degree of formation of their complexes) of gaseous reagents or reagents which would decompose into gaseous products as a result of the reactions is of interest.[170-174]

Although extraction systems as a whole are usually almost reagent free, a small source of salts which might then be transferred to the waste is the operation involving the regeneration of the extractant; this is sometimes carried out to eliminate the microimpurities accumulated after the prolonged use of the extractants, consisting of the products of the decomposition of the extractants which might interfere with the high degree of purification of the valuable elements. A traditional procedure for the elimination of traces of acid decomposition products from NOPC involves washing with solutions of sodium carbonate and alkaline–salt reagents. There has been a growth of interest in the replacement of these operations by sorption or the use of reagents which decompose to gaseous products.[170] In the development of methods for the removal of such impurities, the ideas, considered above, concerning the factors influencing physical partition and the stability of the complexes in extraction systems are employed.

4. The Use of Kinetic Factors. Reactions in the Organic Phase

During the last 10–15 years, the kinetics of extraction have been the subject of numerous studies, which have been surveyed in greatest detail in the monograph of Yagodin and co-workers.[174] The main results of the research into the kinetics has been the discovery of new characteristics of the mechanisms of the processes. For example, it has been shown[175] that one of the causes of the formation of microemulsions of water in the surface layer of the organic phase is the faster mass transfer of the extractable compounds from the aqueous to the organic phase than their dehydration, which then occurs in the surface layer and leads to the liberation of water in the form of the microemulsion. The discovery of the mechanism of the catalytic action of certain impurities or additives on the rate of extraction, which makes it possible to find ways for accelerating the processes, is of great importance.[174,176] Without repeating the numerous examples of the employment of data for the kinetics of extraction in technological schemes, quoted by Yagodin and co-workers,[174] we may note certain additional factors stimulating the development of kinetic studies.

(a) Relatively slow processes occurring when the phases are allowed to stand, for example, the decomposition of reductants when extracts are allowed to stand, which lowers the efficiency of the reductive extraction of plutonium in the scheme designed to separate it from uranium, have been observed.[177]

(b) A greater degree of decomposition of the extractant has been found when the extract was allowed to stand in contact with highly radioactive solutions.[178]

(c) The impurity element is slowly converted into an extractable form on standing in the aqueous phase.[179]

In these cases it is useful to employ types of apparatus with an increased rate of phase separation even if this entails some increase in the complexity of their design or operating costs.

It has been established that, when phosphoryl-containing extractants or substituted ammonium salts are used, the rate of mass transfer under the conditions of vigorous stirring of the phases is sufficiently high and the time required to attain a degree of completion of the process of 90–95% does not usually exceed 1–2 s, i.e. the required phase contact time is short compared with the phase separation time in the gravitional or even in a centrifugal field and no measures are required to accelerate the mass transfer in such systems using apparatus with discrete stages. The kinetics of mass transfer in systems of this kind require investigation mainly in relation to column extractors where additional process acceleration would reduce the height of the equivalent theoretical plate and hence the size of the apparatus. This field of extraction kinetics has so far been little developed and apparently requires more attention in the future.

In a number of instances the slowness of the mass transfer processes also in apparatus with discrete stages has been demonstrated. For example, the extraction by acid reactants is relatively slow. The studies on the use of added "catalysts" accelerating this process, which have been initiated, are of interest for such systems.[180] Sometimes the reason why the process is slow is the low interfacial surface activity of the extractant. For example, the extraction of palladium(II) by dialkyl sulphides is a slow process, because an extractant of this kind is hardly sorbed at the interface, as a result of which its concentration in the reaction zone is very low.[176] In this case the catalyst may even consist of a weak but surface-active extractant, which transfers the palladium(II) compounds into the bulk of the organic phase, where rapid reaction with the dialkyl sulphide can take place.

In most cases the rate of extraction depends on the ratio of the interfacial activities of the extractant and the extractable compound. Nucleophilic extractants are adsorbed from the organic phase at the interface and such adsorption, the extent of which increases with increase in the interfacial activity (as noted above, this has been predicted), accelerates the formation of the extractable solvate. Since metal salts solvated by the nucleophilic extractant are usually surface-inactive, they are readily desorbed from the interface and pass into the bulk of the organic phase. This explains the relatively high rate of extraction of metal salts by the nucleophilic extractant already noted. If the extractant is associated in the organic phase, the degree of its adsorption at the interface is reduced and there is a corresponding decrease of the rate of extraction. Thus the rate of extraction by associated substituted ammonium salts is somewhat lower than the rate of extraction with, for example, tributyl phosphate. The rate of re-extraction of metal salts in such systems is usually somewhat lower than the rate of extraction, probably because the concentration of the surface-inactive solvate at the interface is very low.

The extraction of nucleophilic extractants from the aqueous phase by surface-inactive solvents is a relatively slow process, because, although the adsorption from the aqueous phase at the interface is appreciable, the desorption of the surface-active extractant molecules from the interface to the bulk of the organic phase is hindered.

The slowness of the extraction of many elements by acid extractants may be accounted for qualitatively by the low degree of adsorption of these extractants at the interface as a consequence of the formation of stable associated species and the weak desorption of the extractable compounds from the interface into the bulk of the extractant, because such compounds frequently exhibit a high interfacial activity.[123]

Thus, to a first approximation, the influence of the interfacial properties predicted with the aid of the LFE principle, can be used to explain the characteristic features of the extraction and re-extraction in various technological systems.

The removal of the microimpurity entrained in the extract by washing with an aqueous solution of a complex-forming agent or a reductant is sometimes a slow process. The process is slow because the impurity is wholly in the organic phase, while the reagent is in the aqueous phase. The traditional solution is to increase the phase contact time or the number of stages and the concentration of the reagent. We have shown[181] that the employment of reactions in the organic phase by introducing a reagent soluble in it (before washing) is very effective in such cases. In a homogeneous phase the process involving preparation for washing is much faster than in a heterogeneous system, which in many instances[182] makes it possible to increase the separation factors compared with those obtained as a result of traditional washing by 1–2 orders of magnitude without increasing the contact time or the reagent concentration.

The use of kinetic factors to increase the degree of separation of elements in extraction when there is a significant difference between the rates of their extraction after the appropriate choice of conditions has also attracted the attention of investigators.[33]

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Advances in Catalysis by Heteropolyacids

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The advances in acid catalysis by heteropolyacids are examined and data on the acidity of heteropolyacids are surveyed. The characteristics of homogeneous and heterogeneous acid catalysis by heteropolyacids are discussed and its applied aspects are noted.
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I. INTRODUCTION

Heteropolycompounds (HPC) have come to be widely used as homogeneous and heterogeneous acid and oxidative catalysts by virtue of their unique physicochemical properties.[1-8] They are also of great interest as model systems for the study of fundamental problems of catalysis.[1,4,5] This is due to the available of reliable data on the structure of the HPC, the possibility of the specific variation of their acidity and oxidation potentials, and the similarity of their catalytic action in solution and in the solid state ("pseudo-liquid phase"[1,5]). As a results of studies carried out in the last decade in the USSR and abroad, the scientific principles of the selection of effective HPC catalysts have been formulated. The high Brønsted acidity of heteropolyacids (HPA), greatly surpassing in this respect the usual inorganic acids[4] and traditional acid catalysts,[5] is of fundamental importance for catalysis. The use of HPC as catalysts of oxidation processes is based on the reversibility of their redox reactions and their ability to enter into many-electron oxidation-reduction reactions.[4] Many new catalytic processes in which they participate have been developed, including amongst others a wide variety of processes involving fundamental and fine organic synthesis,[3,4,8] the preparation of hydrocarbons from methanol,[2,7] the photochemical liberation of hydrogen from water.[6] Some of them have already begun to be used in industry abroad, for example, the liquid-phase hydration of propene in the presence of tungsten HPA[9] and the vapour-phase oxidation of methacrolein to methacrylic acid on molybdenum HPC.[5] In the future the number of such processes will undoubtedly increase. Catalysts based on HPC are characterised by a higher activity compared with their existing traditional analogues. With their aid, it is frequently possible to achieve a higher selectivity and also to solve successfully environmental problems.

This communication is devoted to the consideration of the present state of one of the most important aspects of catalysis by HPC—acid catalysis by HPA. Attention is concentrated on the discussion of the acid properties of HPA in solutions and in the solid state, their proton structure, and the characteristic features of the homogeneous and heterogeneous acid catalysis. The use of HPC as oxidation catalysts has been considered in a number of reviews.[3–6]

II. STRUCTURAL CHARACTERISTICS OF HETEROPOLY-ACIDS IN THE SOLID STATE AND IN SOLUTION

HPA and their salts are polyoxo-compounds incorporating anions (heteropolyanions) having metal–oxygen ocathedra MO_6 as the basic structural units. They contain one or several heteroatoms X, which are usually located at the centre of the anion (central atoms). The MO_6 octahedra are linked together and form an extremely stable and compact skeleton of the heteropolyanion (HPAN). The cations may be hydrogen, alkali metal, and other metal ions.[10–12] More than twenty types of structures, incorporating from 4 to 40 metal atoms and from 1 to 9 heteroatoms, are now known for molybdenum, tungsten, vanadium, and niobium HPAN.[12] The commonest compounds, belonging to the saturated 12th series (M : X = 12) are of greatest importance for catalysis. They contain HPAN having Keggin's structure

$$XM_{12}O_{40}^{x-8},$$

where X is the central atom (Si^{IV}, Ge^{IV}, P^{V}, As^{V}, etc.), x the degree of its oxidation, and M is molybdenum or tungsten, which can be partly replaced by other metals. HPA and their acid salts are mainly used in acid catalysis and the neutral salts capable of generating strong acid centres on interaction with the reaction medium are more rarely employed.[7]

The compounds considered are usually obtained by acidifying an aqueous solution containing the salt of the heteroelement and the alkali metal molybdate or tungstate with subsequent isolation of the HPA salt as the hydrate. The acids can be obtained by extracting with ether acidified solutions of the salts and also by ion exchange.[10]

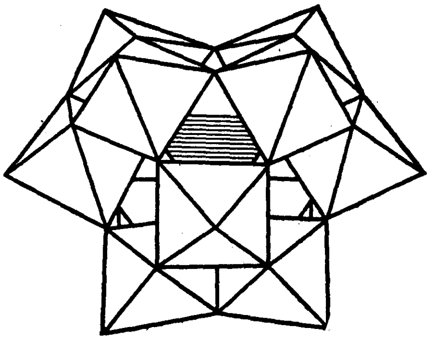

Figure 1. The structure of the heteropolyanion $XM_{12}O^{x-8}$ (α-isomer).[13]

The molecular structure of the 12th series HPC was established by Keggin as early as 1934 by the X-ray diffraction analysis of the hydrates of 12-tungstophosphoric acid.[13] This study played the most important role in the understanding of the laws governing the formation of the HPC structure.[10–12] Keggin's structure for the $XM_{12}O_{40}^{x-8}$ anion (α-isomer) is illustrated in Fig.1. It incorporates the central XO_4 tetrahedron surrounded by 12 MO_6 octahedra having common vertices and edges. The MO_6 octahedra are grouped in four M_3O_{13} triads, which are connected by common vertices. The radius of the HPAN is ~0.6 nm. The anion contains 12 quasi-linear M–O–M linkages between the octahedra forming part of different M_3O_{13} triads, 12 angular $M\overset{O}{\diagup\;\diagdown}M$ bonds between the octahedra within a single triad, 4 X–O–M bonds whereby the triads are joined to the central atom, and 12 terminal M=O bonds. These bonds exhibit characteristic vibration frequencies in the IR spectrum in the range 600–1100 cm^{-1}.[10–12,14]

Keggin's structure is fairly stable. It is preserved in HPC hydration–dehydration and dissolution processes and also on substitution of the metal in the HPAN, on replacement of the outer-sphere cations, and in not too extensive oxidation-reduction reactions.[4,5,10–12]

A less common type of 12th series HPC consists of compounds containing the anions $XM_{12}O_{42}^{x-12}$, where M is molybdenum and X is cerium(IV), uranium(IV), or thorium(IV). They have the Dexter–Silverton structure (Fig.2).[10] The central atom in these compounds is surrounded by 12 oxygen atoms and is located at the centre of the eicosahedron. The MO_6 octahedra are located in pairs on the common face.

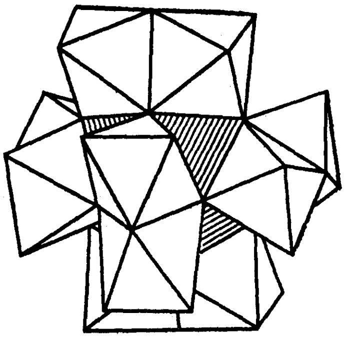

Figure 2. The structure of the hetropolyanion $XM_{12}O_{42}^{x-12}$.[10]

Together with the saturated 12th series HPC, a wide variety of derivatives of unsaturated series are known; the 11th series HPC XM_{11} have a defective Keggin's structure, in which one metal atom is missing, while the 9th series compounds XM_9 are obtained from the 12th series compounds by removing the M_3O_{13} fragment. They dimerise with formation of dinuclear derivatives $X_2M_{18}O_{62}^{x-16}$, having the Dawson structure (Fig.3).[10] The X_2Mo_{18} structure is chiral as a consequence of the slight shift of the Mo atoms relative to one another in two XMo_9 fragments (D_3 symmetry). As a result of this, the X_2Mo_{18} compounds can be used as catalysts in asymmetric synthesis (see below). In contrast to X_2Mo_{18}, the compounds X_2W_{18} possess no chirality and their symmetry is higher, close to the D_{3h} symmetry.[10]

The crystal structure of HPC consists of a three-dimensional lattice made up of HPAN, the cations, and the molecules of the water of crystallisation. In contrast to the rigid molecular structure of the 12-heteropolyanions, it varies within wide limits when their chemical composition and also the conditions of their synthesis and heat treatment are varied.[5,14]

Water-soluble HPC (the acids and salts of many metals) crystallise as hydrates containing a variable number of water molecules (up to 30 and above). Most of the water of crystallisation is readily removed on heating to 100–150 °C.[14]

This process is reversible. It is usually assumed that the main bulk of the water of crystallisation is within the pores of the HPC, as happens in zeolites.[12] The HPAN in the hydrates are not linked to one another and their packing is achieved as a result of the formation of hydrogen bonds with the molecules of the water of crystallisation.[10-12] As a result of this, the HPAN exhibits an appreciable mobility in the crystal matrix.[15] The water molecules in the crystal unit cell form clusters, because the hydrogen bonds between them are stronger than those between the water molecules and the oxygen atoms of the HPAN.[12]

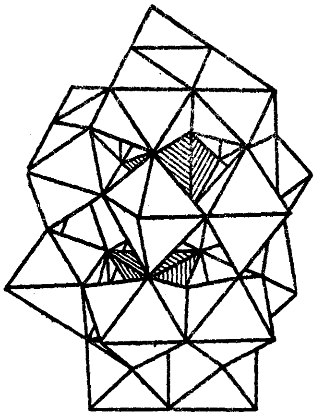

Figure 3. The structure of the heteropolyanion $X_2M_{18}O_{62}^{2x-16}$.[10]

In the dehydration process Keggin's structure of the 12-heteropolyanions is retained, as has been confirmed by the invariance of the IR spectra, but the cell parameters change significantly. Thus, according to X-ray diffraction data, the lattice constant of $H_3[PW_{12}O_{40}].29H_2O$ is 2.33 nm, while $H_3[PW_{12}O_{40}].6H_2O$ has a constant of 1.25 nm.[14] Thus, on dehydration, the unit cell contracts and the distance between neighbouring HPAN diminishes. Consequently, in this case one cannot assume that the water of crystallisation is "zeolitic" in nature. However, the removal of water from the insoluble salts of the acid $H_3[PW_{12}O_{40}]$ hardly alters their crystal structure and in this case the water of crystallisation can be assumed to be "zeolitic".[14]

Like hydrates, HPC form crystalline solvates with molecules of polar organic substances such as alcohols, ethers, ketones, amines, etc. This property plays an important role in heterogeneous catalysis and is manifested in the behaviour of HPA as the "pseudo-liquid phase"[5,7] (see below). The nature of the solvates and the products of their thermal decomposition have been investigated.[16]

The thermal stability of HPC is fairly high. For acids with Keggin's structure, it increases in the sequence $H_4[SiMo_{12}O_{40}]$ < $H_3[PMo_{12}O_{40}]$ < $H_4[SiW_{12}O_{40}]$ < $H_3[PW_{12}O_{40}]$, so that the last acid decomposes at a temperature in excess of 400 °C.[17] The salts are usually more stable than the acids. The thermal stability of the HPC increases in the presence of water vapour.[18]

HPA are as a rule readily soluble in water and water-containing solvents. For example, the solubility of the acid $H_4[SiMo_{12}O_{40}].8H_2O$ at 25 °C is 88 wt.% in water, 86 wt.% in ethyl acetate, and 85 wt.% in diethyl ether.[11] The solubility falls sharply when dehydrated HPA and thoroughly dried non-aqueous solvents are used.[19] HPA do not dissolve in solvents such as benzene, petroleum ether, and chloroform.

The state of the HPC in solution depends on the acidity of the medium, the composition and concentration of the compound, and the nature of the solvent.[4,10,11] Keggin's structure is retained in fairly concentrated solutions but in dilute solutions account must be taken of the possibility of the destruction of the HPAN. The HPAN exist in moderately acid solutions, while in a stronger acid medium they undergo acid hydrolysis with formation of metal oxo-cations. In an alkaline medium hydrolysis with formation of the anions of simple acids of the corresponding heteroatoms and metals takes place. The resistance of the HPAN to hydrolysis in aqueous solutions decreases in the series of metals W > Mo > V [11] and increases in organic media.[4] Recently, significant progress has been achieved in the study of the state of HPC in solutions as a result of the application of ^{31}P, ^{51}V, ^{17}O, ^{183}W, ^{95}Mo, etc. NMR.[10] The NMR method makes it possible to identify HPAN of different structural types and also to detect geometrical isomers without disturbing the equilibrium in the system.

By virtue of their large size, HPAN have a low surface charge density. For this reason, HPA and their salts are almost fully dissociated in aqueous solution and the HPAN are weakly solvated. Nevertheless, saturated HPAN can function as ligands and can give rise to extremely stable complexes with transition and lanthanide metal ions. Several conveniently disposed peripheral M=O groups participate simultaneously in the formation of such complexes. For example, the stability constants of the complexes of anions having the Dexter–Silverton structure, namely $CeMo_{12}O_{42}^{8-}$ and $UMo_{12}O_{42}^{8-}$, with the cations Cu^{2+} and Er^{3+} are 10^5–10^6 litre mol^{-1}.[20,21] The metal cations in these complexes are linked to three oxygen atoms of the HPAN at once, and the HPAN is thus a tridentate macroligand. Heteropolytungstates having Keggin's structure form complexes with the cations Fe^{2+}, Fe^{3+}, MoO_2^{2+}, VO^{2+}, and VO_2^+, characterised by a stability constant of ~10^2 litre mol^{-1}.[22] The complexes of heteropolytungstates with hydrogen peroxide have been discovered and characterised.[23] The complexes of metal cations with defective anions of the type XM_{11} and X_2M_{17},[10] which have a vacancy in Keggin's or Dawson's structure and exhibit a high coordinating capacity, are well known.

The individual metal–oxygen fragments of the compact structure of the HPAN are appreciably mobile and therefore each can be regarded as a discrete ligand. The mobility of the ligands in the HPAN has been established by studying the ^{99}Mo, ^{185}W, and ^{17}O isotope exchange.[24-27] It has been demonstrated with the aid of the ^{32}P isotope that there is no exchange of the central atom in $PMo_{12}O_{40}^{3-}$.[24] The kinetics and mechanism of the substitution of W(VI) in the $SiW_{12}O_{40}^{4-}$ and $PW_{12}O_{40}^{3-}$ anions by the VO^{2+}, VO_2^+, MoO_2^{2+}, Fe^{2+}, and Fe^{3+} cations have been investigated.[22]

III. ACID PROPERTIES OF HETEROPOLYACIDS

Heteropolyacids are strong polybasic acids, greatly surpassing in strength the usual inorganic acids.[4] The basicity of the heteropolyacids $H_{8-x}[X^{x}M_{12}^{VI}O_{40}]$, where M = Mo of W, follows from Keggin's structure and has been demonstrated by numerous direct measurements.[4,11,12]

1. The Acidity of Solid Heteropolyacids

Two types of protons have been found in crystalline HPA:[12,28-30] (1) non-localised hydrated protons bound to one HPAN as a whole and rapidly exchanging with the protons of the water molecules in the hydration shell of the acid; (2) non-hydrated protons localised at the peripheral oxygen atoms of the polyanion. When the water of crystallisation is removed, dehydration takes place and all the protons become localised. Thus water plays an important role in the formation of the proton structure of crystalline HPA.[12] It has been suggested[31] that the oxygen atoms of the angular groups $\mathrm{M}\overset{\mathrm{O}}{\diagup\,\diagdown}\mathrm{M}$ serve as the proton localisation centres because the greatest electron density is concentrated on these particular groups as a consequence of the weaker reversed $d_\pi-p_\pi$ interaction. The majority of the spectroscopic (broad band ^1H NMR and IR) and structural methods do not allow an unambiguous solution of the problem of the site where the protons are localised in polyanions.[12] The ^{17}O NMR method is promising in this respect. Data[26,32] obtained by this method confirm that the O atoms of the angular bridges are protonated in solution. However, one should note that different centres may protonated in crystalline and dissolved HPA.

The hydrated protons in HPA hydrates with a high water content exist in the form of dioxonium ions $H_5O_2^+$ and more complex hydrates $H^+(H_2O)_n$.[12,33,34] This has been established by ^1H NMR and neutron diffraction methods in relation to the hexahydrates of the acids PMo_{12} and PW_{12}. The ion $H_5O_2^+$ appears as a result of the formation of the strong quasi-symmetrical hydrogen bond $H_2O...H^+...OH_2$. In the acid $H_3[PW_{12}O_{40}].6H_2O$, it has an almost planar structure. The O–O distance in the dioxonium ion is significantly reduced owing to the formation of a strong hydrogen bond and amounts to 0.237 nm. The dioxonium ion is linked by hydrogen bonds via the protons of the water molecules to the terminal oxygen atoms of the M=O groups in the HPAN.[34] We may note that, according to the available data,[35] in aqueous solutions of strong acids the simplest stable hydrate is also the dioxonium ion and not H_3O^+. The difference between the H_3O^+ and $H_5O_2^+$ ions is very small and is determined solely by the degree of asymmetry of the $H_2O...H^+...OH_2$ hydrogen bond. If this bond is symmetrical, then the $H_5O_2^+$ complex must be regarded as the dixonium ion and if it is assymetric it should be regarded as the hydroxonium hydrate $(H_3O)^+H_2O$. Apparently such fine differences are not very significant for acid catalysis.

The nature of the acid centres in solid HPA has been established by the method involving the adsorption of bases, mainly pyridine.[1,14,18] Pyridine is adsorbed on strong Brønsted acid centres in the form of the pyridinium ion $C_5H_5NH^+$, while on the Lewis centres it is adsorbed in the form of a complex with a donor–acceptor bond. The difference between the IR spectra of these forms made it possible to establish that the entire pyridine adsorbed on the HPA exists in the form of the pyridinium ion, i.e. the acidity of the HPA is of the Brønsted type.[1,14,18]

The following sequence of crystalline HPA in terms of acid strength has been established by ^1H NMR [30] and pyridine and ammonia thermal desorption[1,14,18,36] methods (the ammonia desorption temperatures in degrees C are indicated under the formulae):

$$\underset{592}{H_3[PW_{12}O_{40}]} > \underset{532}{H_4[SiW_{12}O_{40}]} > \underset{463}{H_3[PMo_{12}O_{40}]} > \underset{423}{H_4[SiMo_{12}O_{40}]}\,.$$

The acidity of phosphoric acids is greater than that of silicic acids and that of tungstic acids is greater than the acidity of molybdic acids. This agrees with the higher negative charge on the oxygen atoms in molybdic acids compared with tungstic acids. The effective charges on the oxygen atoms of the HPA have been determined by X-ray photoelectron spectroscopy.[12] Quantum-chemical calculations have also shown that the charge on the peripheral oxygen atoms increases when W is replaced by Mo.[37]

Crystalline HPA have a stronger acidity than traditional solid acids such as aluminosilicates, H_3PO_4/SiO_2, etc. Thus pyridine adsorbed on $SiO_2-Al_2O_3$ is fully desorbed at 300 °C, while on $H_3[PW_{12}O_{40}]$ it is strongly retained even at a higher temperature in the form of the pyridinium ion.[14] At the same time the number of Brønsted acid centres per unit area of the $H_3[PW_{12}O_{40}]$ and $SiO_2-Al_2O_3$ surfaces is approximately the same.[14]

In many respects, crystalline HPA behave like solutions. This is manifested primarily by the mobility of the elements of their structure. As already mentioned, the HPAN exhibits an appreciable mobility.[15] The HPA protons exchange rapidly with the protons of the molecules of the water of crystallisation.[28,29] Anhydrous HPA exhibit proton conductivity and water vapour accelerates the diffusion of H^+.[30] As in solution, the oxygen atoms of crystalline HPA exchange with the oxygen of water.[1] The rate of such exchange in HPA is much higher than in metal oxides. Crystalline HPA also exchange ^{18}O oxygen with CO_2 and O_2, the rate of exchange diminishing in the sequence $H_2O \gg CO_2 \gg O_2$.[14] The similarity between the molecular structures and the types of behaviour in the crystalline state and in solution makes it possible to treat the mechanisms of homogeneous and heterogeneous catalytic reactions involving them from a single standpoint.

2. The Acidity of Heteropolyacids in Solution

In aqueous solutions there is no adequate justification for subdividing the HPA protons into localised and non-localised. It is more correct to treat HPA as the usual polybasic Brønsted acids in which all the protons are hydrated and equivalent and are linked to the anion as a whole and not to individual basic centres. In solutions all the acid protons are capable of being substituted by other cations, provided that the HPAN is sufficiently stable with respect to alkaline hydrolysis.

Table 1. The dissociation constants of heteropolyacids in water at 25 °C.

pK	$H_5[PMo_{10}V_2O_{40}]$ (Ref.39)	$H_6[PMo_9V_3O_{40}]$ (Ref.39)	$H_7[PV_{12}O_{36}]$ (Ref.38)	$H_8[NpMo_{12}O_{42}]$* (Ref.40)	$H_8[CeMo_{12}O_{42}]$* (Ref.40)	$H_8[UMo_{12}O_{42}]$* (Ref.40)
pK_4	1.16	1.25	3.4	3.24	—	—
pK_5	2,14	1,62	4,9	3.43	2.12	—
pK_6	—	2.00	6.4	3.64	1.98	2,13
pK_7	—	—	7.9	4.28	2.99	3.02
pK_8	—	—	—	5,73	4.16	4.31

*At 20 °C.

In aqueous solution, HPA are strong acids in which the first three protons are fully dissociated. The stepwise character of the dissociation is not observable as a consequence of the levelling influence of the solvent. The subsequent dissociation proceeds stepwise as the pH of the solution is raised. The dissociation constants, starting with K_4, have been measured for certain acids with the Keggin and Dexter-Silverton structures in aqueous solution[38–40] (Table 1).

Non-aqueous solvents have a differentiating effect on the dissociation of the acids. They are more suitable for the investigation of the stepwise dissociation of polybasic acids. It is also significant that in non-aqueous media the HPA are much more stable towards degradation than in aqueous solutions.[4] In ethanol and acetone the first proton and to a large extent also the second proton are fully dissociated in Keggin's structures, while the first and second protons in acids such as $H_3[PW_{12}O_{40}]$ and $H_4[PW_{11}VO_{40}]$ are fully dissociated and the third proton is partly dissociated. In the less polar acetic acid, the HPA behave as comparatively weak 1–1 electrolytes.[4,41,42] Table 2 presents the stepwise dissociation constants of the HPA in acetone and acetic acid and for comparison also the dissociation constants of the usual inorganic acids. Evidently, the HPA are much stronger than the usual inorganic acids such as H_2SO_4, HBr, HCl, HNO_3, and even $HClO_4$. This is of fundamental importance for the application of HPA in acid catalysis. Attention should be drawn to the fact that, in terms of acidity, sulphuric acid, which is a traditional acid catalyst, is inferior to HPA by 2–5 p*K* units. The dependence of the acidity of HPA on their composition is strikingly weak. It is remarkable that the nature of the central atom has almost no influence despite the fact that the strengths of the corresponding simple acids differ appreciably (thus H_3PO_4 and H_4SiO_4 have $pK_1 = 2.12$ and 9.7 respectively in water[45]). Heteropolyacids are significantly stronger than the corresponding simple acids, which are weak or moderately strong.

Table 2. The dissociation constants of heteropolyacids in acetone and acetic acid.

Acid	Acetone			Acetic acid
	pK_1	pK_2	pK_3	pK_1
$H_3[PW_{12}O_{40}]$	1.6	3.0	4.0	4.8
$H_4[PW_{11}VO_{40}]$	1.8	3.2	4.4	4.7
$H_5[PW_{10}V_2O_{40}]$	—	—	—	4.8
$H_4[SiW_{12}O_{40}]$	2.0	3.6	5.3	5.0
$H_3[PMo_{12}O_{40}]$	2.0	3.6	5.3	4.7
$H_4[PMo_{11}^{VI}Mo^{V}O_{40}]$	2.1	3.7	5.5	—
$H_4[PMo_{11}VO_{40}]$	2.1	3.7	5.6	4.7
$H_4[SiMo_{12}O_{40}]$	2.1	3.9	5.9	4.8
$H_4[GeW_{12}O_{40}]$	—	—	—	4.3**
$H_5[GeW_{11}VO_{40}]$	—	—	—	4.7**
$H_6[GeW_{10}V_2O_{40}]$	—	—	—	4.6**
$HClO_4$	—	—	—	4.9***
HBr	—	—	—	5.6***
H_2SO_4	6.6*	—	—	7.0***
HCl	4.3*	—	—	8.4***
HNO_3	9.4*	—	—	10.1***

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*From Pawlak et al.[43]

**From Polotebnova et al.[44]

***From Porcham and Engelbrecht.[46] The p*K* not marked with asterisks were taken from Kozhevnikov and co-workers.[41,42]

The difference between the strengths of the HPA and the usual acids can be most simply explained within the framework of the electrostatic theory taking into account the size of the anions and the number of oxygen atoms available for the delocalisation of the charge of the anion.[4,41,42] Since the HPAN are much larger than the anions of the usual acids, the energy of the proton bond in the HPA should be lower and their dissociation constants should be higher compared with the usual acids. Furthermore, the greater the degree of delocalisation of the charge of the anion, the smaller the effective negative charge on its individual basic proton-accepting centres, and hence the weaker the attraction of the proton to the acid anion. The formal negative charges of the HPAN $PM_{12}O_{40}^{3-}$ and $SiM_{12}O_{40}^{4-}$ are identical with the charges on the anions of the corresponding simple acids PO_4^{3-} and SiO_4^{4-}, but the charge per outer oxygen atom is 9 times smaller in the HPA than in the phosphate and silicate ions. As a result of this, the acids $H_{8-x}[XM_{12}O_{40}]$ are much stronger than $H_{8-x}[XO_4]$. An interesting analogy between the properties of the HPA and inorganic acids having the general formula $XO_n(OH)_m$, where X is a group IVA–VIIA element, is noteworthy. These acids are remarkable because their strength increases with increase in *n* and depends little on *m* for constant *n*.[47]

The weak influence of the composition of the HPA on their acidity nevertheless obeys a definite rule, which is clearer in polar solvents. In solvents of low polarity, for example, in acetic acid, there is a possibility of the influence by ion association. The series based on the acid strengths of the HPA in acetone is:[4,42]

$$H_3[PW_{12}O_{40}] > H_4[PW_{11}VO_{40}] > H_4[SiW_{12}O_{40}] \simeq H_3[PMo_{12}O_{40}] >$$
$$> H_4[PMo_{11}^{VI}Mo^{V}O_{40}] \simeq H_4[PMo_{11}VO_{40}] > H_4[SiMo_{12}O_{40}]\ .$$

A similar sequence has been observed from the variation of the chemical shifts of the proton of chloral hydrate in the presence of HPA, obtained using nitrobenzene as the solvent. Thus the acidity series in solutions agrees well with the series found for solid acid hydrates. This agreement is reasonable, because the HPA behave in approximately the same way in the solid state and in solution.

The acidity diminishes when the HPA is reduced and when Mo or W is replaced by V and also on replacement of the central P atom by Si.

In all the cases enumerated, the decrease in acidity when the composition of the HPA is altered is accompanied by an increase in its basicity (the number of equivalent protons bound to the HPAN). The above dependence of the dissociation constants of HPA on their basicity agrees with the prediction of the electrostatic theory. By treating the HPAN as conducting spheres, with a charge equal to the basicity of the HPA, and the protons as positive point charges, it can be shown that any change in composition leading to an increase in the basicity of the HPA entails a decrease in the dissociation constants.[42] We may note that the substitution of Mo by W in the HPAN increases the dissociation constant but does not alter the basicity of the acid. However, in this case there is a correlation between the acidity and the effective charge on the peripheral oxygen atoms of the anion.

The splitting off of a proton from the acid can be represented as an ionisation process—dissociation with the intermediate formation of an ion pair:[48]

$$HPA \overset{K_i}{\rightleftarrows} HPAN^- \| H^+ \overset{K_d}{\rightleftarrows} HPAN^- + H^+\ .$$

It has been established that the HPA in solution are almost fully ionised ($K_i \gg 1$) and exist in the form of solvate-separated ion pairs.[41,42] Thus the specific features of the acid properties of the HPA are determined by the weak electrostatic bond between the proton and the anion in the ion pair. The fruitfulness of electrostatic ideas in the chemistry of HPC, owing to the large amount of ionic character in the bond between the cations and the polyanions and the weak solvation of the HPC, must be emphasised.

Concentrated HPA solutions are of great interest for catalysis. The acidity of concentrated $H_3[PW_{12}O_{40}]$ solutions is greater than the acidity of solutions of sulphuric and perchloric acids having the same concentration. The difference between the H_0 is 1–1.5 units.[49] Presumably the values of *H* are similar for acids of different composition, because in dilute solutions the dissociation constants of HPA depend only slightly on composition.

Using the concepts of hard and soft acids and bases, one can say that the HPAN are soft bases, which interact weakly with the hard acid H^+. According to Izumi et al.,[19] acids can be arranged in the following sequence in terms of their softness:

$$SiW_{12}O_{40}^{4-} > GeW_{12}O_{40}^{4-} > PW_{12}O_{40}^{3-} > PMo_{12}O_{40}^{3-} >$$
$$> SiMo_{12}O_{40}^{4-} > NO_3^- > p\text{-}MeC_6H_4SO_3^- > SO_4^{2-}.$$

3. Relation between the Oxidative and Acid Properties of Heteropolycompounds

HPC are many-electron oxidants. The addition of electrons increases the basicity of the HPAN and may be accompanied by protonation. The reduction of the Mo and W HPAN can be represented by the following equation taking into account protonation:

$$XM_{12}^{VI}O_{40}^{x-8} + ne^- + mH^+ \rightarrow H_mXM_{12-n}^{VI}M_n^VO_{40}^{x+m-n-8}$$

where $m \leq n$.[4,10,50] Hence the oxidation potential of the HPAN is

$$E = E_0 + \frac{RT}{nF} \ln \{XM_{12}^{VI}O_{40}^{x-8}\}\{H^+\}^m/\{H_mXM_{12-n}^{VI}M_n^VO_{40}^{x+m-n-8}\},$$

where E_0 is the standard redox potential, F is the Faraday, and the formulae in braces represent the ionic activities.

Table 3. The redox potentials of Keggin's structure of heteropolycompounds in aqueous solution.

Redox system	n_e	E_0, V	Refs.
	V (V) → V (IV)		
$PV^VW_{11}/PV^{IV}W_{11}$	1	0.78	[53]
$PV^VMo_{11}/PV^{IV}Mo_{11}$	1	0.68	[54]
$PV_2^VMo_{10}/PV_2^{IV}Mo_{10}$	2	0.71	[54]
$PV_3^VMo_9/PV_3^{IV}Mo_9$	3	0.71	[54]
$PV_4^VMo_8/PV_4^{IV}Mo_8$	4	0.71	[54]
	Mo (VI) → Mo (V)		
$PMo_{12}^{VI}/PMo_9^{VI}Mo_3^V$	3	0.65	[55]
$SiMo_{12}^{VI}/SiMo_9^{VI}Mo_3^V$	3	0.63	[55]
	W (VI) → W (V)		
$BW_{12}^{VI}/BW_{11}^{VI}W^V$	1	−0.36	[56]
$GeW_{12}^{VI}/GeW_{11}^{VI}W^V$	1	−0.02	[56]
$SiW_{12}^{VI}/SiW_{11}^{VI}W^V$	1	−0.05	[56]
$PW_{12}^{VI}/PW_{11}^{VI}W^V$	1	0.15	[56]
	Co (III) → Co (II)		
$Co^{III}W_{12}/Co^{II}W_{12}$	1	1.0	[57]

Remarks. The O atoms and charges have been omitted from the formulae; n_e is the number of electrons transferred and E_0 is expressed relative to the normal hydrogen electrode.

The quantities E_0 are as a rule unknown owing to the lack of data on the HPAN equilibria in solution. One uses instead the corresponding formal redox potentials, which depend on the pH and the HPAN concentration.[50] It is seen from the last equation that the oxidation potential of the HPAN depends on the acidity of the medium, at least in the pH range where the anion is protonated on reduction. Tungsten anions with Keggin's structure may have a charge up to −6 without the addition of protons on reduction in an acid aqueous solution (pH ≤ 1) by virtue of the high acidity of the corresponding acids.[51] In non-aqueous media, their charge is much smaller.

The oxidation potential of the HPC depends on the nature of both the metals and the central atom[4,50,52] (Table 3). The oxidation potential diminishes in the series of metals V > Mo > W. The central atom (a constant electrovalence ion) influences the redox potential via the change in the charge of the HPAN: the higher the charge of the anion, the lower the oxidation potential.[4,50,52] The dependence of the redox potential on the charge of the anion is frequencly linear and can be predicted with the aid of electrostatic theory.[52]

It has been demonstrated by the temperature-programmed reduction method that the ease of reduction of solid HPA by hydrogen diminishes in the sequence $PmO_{10}V_2 \cong SiMo_{12} \geqq PmO_{12} \cong PmO_6W_6 > PmO_2W_{10} > PW_{12} \cong SiW_{12}$, and the ease of reduction of salts of 12-molybdophosphoric acid diminishes in the sequence $Ag^+ > Cu^{2+} > Ni^{2+}$.[5,58] The process is appreciably facilitated if a mixture of the acids with the Pd/C catalyst is reduced. Thus the capacity of solid HPA for reduction is fairly well correlated with the redox potentials in solution.

The question of the relation between the oxidative and acid properties of HPA is important for their use as acid catalysts. Comparison of the dissociation constants and oxidation potentials of HPA (Tables 2 and 3) shows that there is no correlation between them. At the same time, one must bear in mind that the dissociation constants of HPA diminish when they are reduced. Thus the catalytic activity of HPA should depend on the reducing capacity of the reaction medium.

Data on the kinetics of the redox reactions of HPAN with various one-electron reductants and oxidants are of interest in this connection. It has been established[59] that the observed kinetics agree satisfactorily with the Marcus theory. Thus this theory can be used to predict the stability of HPA in a reducing medium under the conditions of acid catalysis.

IV. ACID CATALYSIS BY HETEROPOLYACIDS

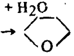
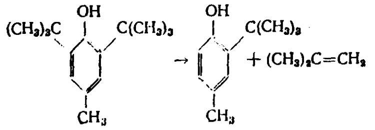
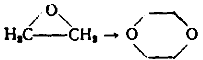
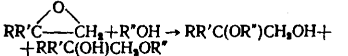
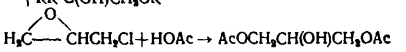
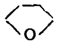
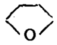
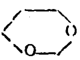
Heteropolyacids have long been used in catalysis,[3,10,11] but systematic studies in this field began comparatively recently. The likely usefulness of HPA as acid catalysts is due to their high Brønsted acidity, which is superior to that of the usual catalysts. Since HPA are readily soluble in water and oxygen-containing solvents and their stability in the solid state is fairly high, they are used as both homogeneous and heterogeneous catalysts. The W and Mo HPA have acceptable technological characteristics. In contrast to the usual inorganic acids, they are non-toxic and involatile, have no smell, and are stable on prolonged storage. Although HPA are much more expensive than acids such as sulphuric and hydrochloric, their use is frequently economically justified because of the high efficiency of their catalytic action.

Tungstic acids are the preferred catalyst in the series of HPA[4] because of their higher acidity, hydrolytic and thermal stability, and lower oxidation potentials compared with the Mo and V acids. In heterogeneous catalysis, one uses, together with HPA, their salts with cations such as Ag^+, Cu^{2+}, Pd^{2+}, Al^{3+}, etc.[7] The mechanism of the formation of acid centres in such systems is examined below. The strength and number of acid centres of HPA catalysts can be regulated by selecting the outer-sphere cation, by replacing the central atom and the metal in the structure of the polyanion, and also by employing carriers of different nature and by varying the concentration of the acid on the carrier.[5] In both homogeneous and heterogeneous catalysis by heteropolyacids, the

Brønsted rule usually holds satisfactorily: the catalytic activity is correlated with the strength of the acid centres of the catalyst.

Table 4 presents examples of reactions catalysed by HPA, many of which are of practical interest. HPA are frequently superior to the traditional acid catalysts as regards not only activity but also selectivity. This is because they make it possible to carry out the process under milder conditions. Furthermore, by virtue of the inertness of the anion, HPA do not enter into side reactions with organic reagents, in the manner characteristic of the usual inorganic acids (sulphonation, chlorination, etc.).[4]

Table 4. Acid catalystis by heteropolyacids.

Reaction	Catalyst	T, °C	α, %	A	Refs.
Hydration–dehydration					
$RCH{=}CH_2 + H_2O \rightarrow RCH(OH)CH_3$	PW_{12}, SiW_{12}, PMo (hom.)	170—350	95—99	2—4	[9]
$C_6H_5C{\equiv}CH + H_2O \rightarrow C_6H_5COCH_3$	PW_{12}, PMo_{12} (hom.)	60	—	100	[3, 60]
$CH_3CH(OH)CH_3 \rightarrow CH_2{=}CHCH_3 + H_2O$	PW_{12} (het.)	150	100	100	[61]
Esterification					
$RCH{=}CH_2 + R'COOH \rightarrow RCH(OOCR')CH_3$	PW_{12} (hom.)	20—140	100	30—90	[62]
$(CH_3)_2C{=}CH_2 + CH_3OH \rightarrow (CH_3)_3COCH_3$	PW_{12}/SiO_2, PW_{12}/C, SiW_{12}/C	90	100	300	[63, 64]
$t\text{-}C_4H_9OH \rightarrow (t\text{-}C_4H_9)_2O + H_2O$	PW_{12}/C, SiW_{12}/C	106	—	—	[65]
$HOCH_2CH_2CH_2CH_2OH \rightarrow$  $+ H_2O$	SiW_{12}, PW_{12}, PMo_{12} (hom.)	160	—	3	[66]
$C_2H_5OH + HOAc \rightarrow C_2H_5OAc + H_2O$	PW_{12}/C, SiW_{12}/C	120—150	96—100	>2	[36]
$n\text{-}C_4H_9OAc + C_2H_5OH \rightarrow C_2H_5OAc + n\text{-}C_4H_9OH$	PMo_{12}, PW_{12} (hom.)	110	—	4—10	[67]
Decomposition					
$C_6H_5(CH_3)_2COOH \rightarrow C_6H_5OH + CH_3COCH_3$	PMo_{12} (hom.)	25—60	>99	>100	[68]
$HCOOH \rightarrow CO + H_2O$	PW_{12} (het.)	150	100	—	[69]
$CH_3CH(CH_3)COOH \rightarrow CH_2{=}CHCH_3 + CO + H_2O$	PW_{12}, SiW_{12} (het.)	240	100	4	[70]
Nitration					
$C_6H_6 + NO_2 \rightarrow C_6H_5NO_2 + NO + H_2O$	PW_{12}/SiO_2	270	—	—	[66]
Alkylation–dealkylation					
$C_6H_6 + CH_3CH{=}CH_2 \rightarrow C_6H_5CH(CH_3)_2$	SiW_{12}/SiO_2	150	73	60	[71]
$C_6H_5HC(CH_3)_2 \rightarrow C_6H_6 + CH_3CH{=}CH_2$	PW_{12} (het.)	250	—	—	[69]
$C_6H_5CH_3 + CH_3OH \rightarrow C_6H_4(CH_3)_2 + H_2O$	PW_{12} (het.)	250	—	—*	[5, 72]
	PW_{12}, SiW_{12} (hom.)	118	97	>100	[73]
Reactions of epoxides					
	SiW_{12}/SiO_2, $SiMo_{12}/SiO_2$	100—260	—	—	[74]
 $RR'\overset{O}{C}{-}CH_2 + R''OH \rightarrow RR'C(OR'')CH_2OH + RR'C(OH)CH_2OR''$	PW_{12}, PMo_{12}, SiW_{12} (hom.)	50	95—97	—	[75]
 $H_2\overset{O}{C}{-}CHCH_2Cl + HOAc \rightarrow AcOCH_2CH(OH)CH_2OAc$	PW_{12}, PMo_{12}, SiW_{12}, GeW_{12} (hom.)	30	~100	10^3**	[19]
Acetolysis					
 $+ HOAc \rightarrow AcOCH_2CH_2CH_2CH_2OAc + H_2O$	PW_{12}, SiW_{12}, PMo_{12} (hom.)	95	—	>100**	[19]
$(C_4H_9)_2O + HOAc \rightarrow C_4H_9OAc + H_2O$	PW_{12}, SiW_{12}, PMo_{12} (hom.)	118	—	100**	[19]
 $+ Ac_2O \rightarrow (AcOCH_2CH_2CH_2CH_2)_2O$	SiW_{12}, PW_{12}, GeW_{12} (hom.)	50	89—95	$>10^3$	[19]
Isomerisation					
But-1-ene → but-2-ene	PW_{12} (het.)	—	—	—	[61]
cis-But-2-ene → *trans*-but-2-ene	PW_{12} (het.)	25—100	—	—	[69]
o-Xylene → *p*-xylene + *m*-xylene	PW_{12} (het.)	300	—	—	[76]
n-Alkane → isoalkane	$Pd - PW_{12}/SiO_2$	210	87	—	[77]
Condensation					
$CH_3COCH_3 \rightarrow 1,3,5\text{-}(CH_3)_3C_6H_3$	PW_{12}, PMo_{12}, SiW_{12} (hom.)	25	40—55	—	[78]
$C_6H_5CH{=}CH_2 + CH_2O \rightarrow C_6H_5{-}$ 	PMo_{12}, PW_{12} (hom.)	45	—	50	[79]
$n\,C_6H_5CH_2OH \rightarrow {-}({-}C_6H_4CH_2{-})_n{-} + (n-1)H_2O$	PW_{12} (hom.)	25	—	—	[5, 80]
Reactions of methanol and CO					
CH_3OH → olefin + alkane	PW_{12}, SiW_{12} (het.)***	300	—	—	[2, 7]
$CO + H_2O \rightarrow HCOOH$	PMo_{12}, SiW_{12} (het.)	200—300	—	—	[81]
$CO + ROH \rightarrow RCOOH$	PMo_{12}, SiW_{12} (het.)	200—300	—	—	[81]
Polymerisation and oligomerisation					
$n\,RCH{=}CH_2 \rightarrow {-}({-}CHR{-}CH_2{-})_n{-}$	PW_{12}/Al_2O_3	300	—	—	[82]

Notation: XM_{12} are the heteropolyacids $H_{8-x}[XM_{12}O_{40}]$ and in certain cases their salts; hom. = homogeneous catalytic systems and het. = heterogeneous catalytic systems; T is the temperature; A is the ratio of the catalytic activity of the HPA to the activity of an inorganic acid (H_2SO_4) in homogeneous reactions or of aluminosilicate in heterogeneous reactions; α is the selectivity.

*The aluminosilicate exhibits an appreciable activity only above 400 °C.[5,72]

**The activity of the HPA in relation to toluene-p-sulphonic acid.

***Together with the acids, the Ag^+, Cu^{2+}, and Al^{3+} salts are active.

1. Homogeneous Acid Catalysis

In this Section attention is concentrated on the following questions: (a) comparison of HPA and the usual inorganic acids in terms of their catalytic activity and selectivity; (b) dependence of the activity of HPA on their composition; (c) relation between the activity of HPA and their acidity; (d) the influence of the oxidative properties of HPA on their catalytic action.

The hydration of lower olefins is the first example of the practical application of HPA in an acid catalysed process.[9] The application of HPA on carriers as heterogeneous catalysts of the hydration of olefins has been known for a long time. They are more active than the industrial H_3PO_4/SiO_2 catalyst and are not removed by entrainment.[83] In the homogeneous process developed comparatively recently,[9] olefins ranging from ethylene to butene are converted into alcohols with a selectivity of 95–99% at 170–350 °C and pressures in the range 10–30 MPa in the presence of 10^{-5}–10^{-3} M aqueous solutions of $H_4[SiW_{12}O_{40}]$, $H_3[PW_{12}O_{40}]$, $H_5[BW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiMo_{12}O_{40}]$, and their soluble salts. In conformity with their strength, the catalytic activity of HPA is higher than those of sulphuric and nitric acids.[79] The main advantage of the homogeneous hydration of olefins compared with the heterogeneous process is the attainment of higher degrees of conversion of the olefin as a result of the increased concentration of water and the use of a higher pressure. Data concerning industrial liquid-phase hydration of propene under the influence of HPA have been published recently.[9]

The addition of carboxylic acids to olefins (esterification of olefins) proceeds smoothly in solution in the presence of 10^{-4}–10^{-2} M tungsten and molybdenum HPA at 20–140 °C with a selectivity of ~100% in relation to esters of secondary alcohols.[4,62] Sulphuric acid, whose acidity is lower, is less active than HPA by a factor of 30–90.[62] The activity of tungstic acid is higher by a factor of 2–2.5 than that of molybdic acids, despite the virtual identity of their dissociation constants, which is due to the difference between the oxidation potentials of the acids. Molybdic acids, which are stronger oxidants, are reduced during the reaction by the components of the reaction mixture and lose their acidity, while tungstic acids are not reduced, because their oxidation potentials are significantly lower.

The dealkylation of derivatives of 2,6-di-t-butylphenol to 2-t-butylphenols is a key stage in the synthesis of widely used phenolic antioxidants. The acids PW_{12} and SiW_{12} are highly active homogeneous and heterogeneous catalysts of this reaction.[73,84,85] The heterogeneous process proceeds at 130–150 °C in the presence of the catalyst (less than 1%) in the melt of the substrate.[84,85] Molybdic acids are raidly deactivated as a result of their reduction by the reaction medium. HPA are tens of times more active than heterogeneous catalysts such as ion-exchange resins, aluminosilicates, aluminium sulphate, etc. The homogeneous process is even more effective. In solutions in acetic acid, dealkylation takes place already at 80 °C.[73] The catalytic activity of HPA is correlated with the acidity and exceeds by a factor greater than 100 the activity of sulphuric acid.

The transesterification of butyl acetate to form ethyl acetate takes place in solution in ethanol at 110–130 °C in the presence of 10^{-4}–10^{-2} M tungsten or molybdenum HPA.[67] In this reaction, the HPA is 4–10 times more active than sulphuric acid. Contrary to expectation, molybdic acids proved to be more active in this instance than tungstic acids. In the course of the reaction, the Mo acids are reduced and probably partly decompose. The true catalyst apparently consists of alkoxide complexes of molybdenum formed on decomposition of the HPA. In conformity with this hypothesis, the order of the reaction with respect to the molybdenum HPA is less than unity (the order with respect to tungstic acids is unity). We may note that titanium and zirconium alkoxide complexes are known to catalyse effectively esterification reactions.[86] The reduction and decomposition of molybdic acids have also been observed in the acetolysis reactions of esters.[19]

The acid decomposition of cumenyl hydroperoxide is the basis of the commonest industrial method of synthesis of phenol and acetone. Many homogeneous and heterogeneous catalysts have been proposed for this reaction, but only sulphuric acid has found practical application, although in its presence the process is insufficiently selective and yields phenolic waste water.[87] HPA are very active and selective homogeneous catalysts of the decomposition of cumenyl hydroperoxide.[68,88] Compared with sulphuric acid, they reduce the yield of the phenolic resin and the amount of waste water and increase the quality of the phenol obtained. The reaction rate constants k is correlated with the acidity of the HPA (in acetone at 25 °C [68]):

Catalyst	PW_{12}	$PW_{11}V$	PMo_{12}	SiW_{12}	$PMo_{11}V$	$SiMo_{12}$
$10^4 k$, s^{-1}	8.0	6.4	6.3	5.8	4.2	3.5
pK_a	3.0	3.2	3.6	3.6	3.7	3.9

Sulphuric acid is less active by 2–3 orders of magnitude than HPA.

The most selective catalyst of the decomposition of cumenyl hydroperoxide is 12-molybdophosphoric acid.[88] Tungstic acids are significantly less selective. It is most probable that this is due to the difference between the oxidative properties of the molybdic and tungstic acids. The point is that, in the presence of the hydroperoxide, which is a powerful oxidant, the HPA are in the oxidised state. After the completion of the decomposition of the hydroperoxide, the reaction medium becomes reducing and the molybdenum HPA are rapidly reduced in it and lose their catalytic activity. Tungsten HPA and the usual inorganic acids are not reduced and continue to catalyse side condensation reactions after the decomposition of the hydroperoxide has been completed. Thus the oxidative properties of HPA may also play a positive role in acid catalysis under certain conditions.

A selective semi-industrial method of synthesis of methyl methacrylate by the homogeneous esterification of methacrylic acid with t-butyl methyl ether (TBME) in the presence of Mo and W heteropolyacids at 110–150 °C has been developed:[89]

$$H_2C{=}C(CH)_3COOH + (CH_3)_3COCH_3 \rightarrow$$
$$\rightarrow H_2C{=}C(CH_3)COOCH_3 + H_2C{=}C(CH_3)_2\ ,$$

The initial stage is the decomposition of TBME to methanol and isobutene. The isobutene dimer is formed as a side product, but its yield can be appreciably reduced by the continuous removal of isobutene from the reactor.

A new interesting aspect of catalysis by HPA is asymmetric synthesis. It has been found recently that the chiral acid $H_6[P_2Mo_{18}O_{62}]$ can be used as the catalyst of the asymmetric polycondensation of benzyl alcohol.[90] In the presence of the l-brucine-$H_6[P_2Mo_{18}O_{62}]$ homogeneous system, benzyl alcohol is converted into an optically active polybenzyl:

$$nC_6H_5CH_2OH \rightarrow -(-C_6H_4CH_2-)_n- + (n-1)H_2O.$$

In the presence of the non-chiral acid $H_6[P_2W_{18}O_{62}]$, an optically inactive polybenzyl is formed.

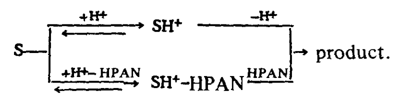
The homogeneous reactions catalysed by HPA are usually of first order with respect to the substrate S. The order with respect to the catalyst depends on the ionising capacity of the solvent. Thus, in media where the degree of dissociation of the HPA is low, the reactions are of first order. For example, the rates of the reactions involving the esterification of olefins and the dealkylation of derivatives of 2,6-di-t-butylphenol in acetic acid[62,73] are described by the expression:

$$v = k[\mathrm{HPA}][\mathrm{S}].$$

In more polar solvents, where the degree of dissociation of the HPA is appreciable, the process frequently takes place in accordance with the kinetic equation

$$v=(k_1[\mathrm{H}^+]+k_2[\mathrm{H}^+\text{—HPAN}])[\mathrm{S}],$$

where H^+–HPAN is the acid heteropolyanion. Examples of such reactions are the decomposition of cumenyl hydroperoxide into phenol and acetone in acetone (H^+–HPA = $H_2PMo_{12}O_{40}^-$),[68] the hydration of isobutene,[3,79] and the cyclisation of butane-1,4-diol to tetrahydrofuran[66] in aqueous solution (H^+–HPA = $HSiW_{12}O_{40}^{3-}$). In this case, the reaction proceeds via two pathways: specific catalysis by the H^+ ion and general catalysis by the HPAN:



Thus HPA are more active as homogeneous catalysts than the usual acids, especially sulphuric acid. This makes it possible to carry out the catalytic processes at a lower catalyst concentration, which frequently increases the selectivity and makes it possible to reduce the amount of waste water in the neutralisation of the catalyst.

2. Heterogeneous Catalysis

(a) *General characteristics.* In heterogeneous catalysis, HPA and their salts are used as massive and deposited catalysts. The best carriers are neutral supports—silica gel and activated charcoal. Basic carriers, such as Al_2O_3 and MgO, are unsuitable, because they neutralise the HPA.[36] The properties of catalysts based on the salts depend significantly on the nature of the metal cation, the degree of substitution of hydrogen in the acid by the metal, and the solubility of the salt. The temperature at which the HPA catalysts are used does not as a rule exceed 300–350 °C, which is within the limits of the thermal stability of tungstic acids. Since HPA and the water soluble salts are highly hydrated, they are subjected to a preliminary heat treatment *in vacuo* at 100° to 300 °C in order to remove the water of crystallisation. Such heat treatment does not disrupt the structure of the HPAN. Evacuation of the HPC at 130 °C for 1 h lowers the amount of water to 1–2 molecules per HPAN.[69] The insoluble salts are hydrated to a much lesser extent. Their water is zeolitic in character and is readily removed by evacuation at 25 °C.[14]

The acids in massive form and their soluble salts are characterised by a low specific surface (1–5 $m^2\ g^{-1}$), which depends little on the heat treatment conditions.[69,91] The specific surface of insoluble caesium salts reaches 100–200 $m^2\ g^{-1}$ The acid caesium salts $Cs_{3-x}H_x[PW_{12}O_{40}]$ (x = 0.15 to 0.5), which have a large surface area, are of interest as insoluble acid catalysts.[5,92] They are distinguished by a higher thermal stability than the initial acids.[5]

The porosity of massive specimens of the PmO_{12} and PW_{12} acids is insignificant. Thus $H_3[PMo_{12}O_{40}]$ has a pore volume of 0.026 $cm^3\ g^{-1}$ at 25 °C and a wide distribution of the pore sizes with respect to radius. After vacuum treatment at 110 °C, the pore volume remains unchanged but a narrow peak, corresponding to a radius of ~2 nm, appears on the pore size distribution curve. Such pores are formed as a result of the change in the crystal structure of the acid on dehydration, which leads to the appearance of cavities and the contraction of the unit cell. After evacuation at 450 °C, the peak vanishes; the pore distribution again becomes broad, which can be accounted for by the further mutual approach of the HPAN.[93]

The study of the PW_{12} and SiW_{12} acids deposited on silica gel by X-ray diffraction showed that the HPA phase on the carrier surface is formed when its content is ~20 wt.%.[36] According to ammonia thermal desorption data, the strength of the HPA on silica gel diminishes, as for the massive acids, on passing from PW_{12} to SiW_{12}, and is independent of its concentration on the carrier.[36] HPA on activated charcoal exhibit high activity and are not washed off by water and organic solvents.[65] Such catalysts are promising for processes in suspension. The decomposition of tungsten HPA was observed when these were deposited on alumina even when the basicity of the Al_2O_3 had been reduced by preliminary treatment with HCl.[36]

The activity of deposited catalysts usually increases with increase in the content of the HPA to 15–30 wt.% (which corresponds to approximately monolayer coverage) and is subsequently independent of the latter.[36,66] The activity of the deposited catalysts calculated per acid molecule is much lower than the activity of the massive acid specimens. This applies to reactions such as the alkylation of benzene with ethylene, the esterification of acetic acid with ethanol, the dehydration of 2-propanol,[36] the vapour-phase nitration of benzene,[66] etc.

(b) *The "pseudo-liquid phase".* The water-soluble HPC exhibit a high affinity for the molecules of polar substances such as alcohols, ketones, ethers, esters, amines, etc. Large amounts of these substances are sorbed in the bulk of the crystalline HPC with formation of solvates. This phenomenon should not be confused with adsorption in the micropores of the usual sorbents.[1,5,7] Table 5 presents data for the absorption and adsorption of polar and non-polar substances by the acid $H_3[PW_{12}O_{40}]$. The total degree of sorption of the substance at 25 °C and the amount which is irreversibly retained after evacuation at 25 °C are indicated. For polar molecules, the latter corresponds to the presence of 50–100 layers of the sorbate on the $H_3[PW_{12}O_{40}]$ surface. Oxygen-containing compounds are almost fully desorbed at 100–150 °C, while nitrogen derivatives require the use of higher temperatures. The degree of sorption of non-polar hydrocarbons (alkanes, olefins, arenes) is insignificant. They are adsorbed only on the HPA surface.

Table 5. The sorption of different substances by the acid $H_3[PW_{12}O_{40}]$ at 25 °C.[5]

Substance	Sorption*	
	irreversible	total
Pyridine	6.0	9
Ammonia	3.2	4.3
Methanol	2.2	>10
Isopropyl alcohol	6.3	>10
Ethylene	0,03	0.04
But-1-ene	0.2	0.25
Benzene	0,1	0.5

*The number of sorbed molecules of the given substance per HPA molecule.

By virtue of the rapid absorption of polar molecules, the catalytic reactions can occur not only on the surface but also on the bulk of the massive HPA. In relation to polar substances, solid HPA behave similarly to highly concentrated solutions, i.e. all the acid protons and not only the surface protons participate in the catalytic reaction. This phenomenon, which is unusual for heterogeneous acid catalysis and is characteristic of massive HPA, is described by the term "pseudo-liquid phase".[1,5] The ability of crystalline HPA to effect the catalytic reactions of polar substances in the bulk of the catalyst, like the reactions in homogeneous systems, is implied.

In contrast to polar molecules, non-polar reagents are incapable of being absorbed in the bulk of the HPA; they interact only with the surface of the catalyst. Soluble salts of HPA also possess the property of the "pseudo-liquid phase". Insoluble salts, which do not absorb polar molecules, possess no such property.

In terms of the catalytic properties in relation to the molecules of polar substances, massive HPA resemble zeolites to some extent. In both cases, virtually all the acid centres of the catalyst are accessible: in the HPA as a result of the absorption of the substrate in the bulk phase and in zeolites as a result of the high internal surface area. However, whereas in the case of HPA this is true only of polar molecules, in a zeolite this is true of any molecules whose dimensions do not exceed the diameter of the zeolite channels. In contrast to zeolites, HPA do not have sufficiently pronounced molecular-sieve properties, because they do not have a rigorously ordered porous structure.

Several studies have been devoted to the "pseudo-liquid phase".[1,5,7,94–98] The dehydration of alcohols (ethanol, 2-propanol, 2-butanol),[69,94] the conversion of methanol into hydrocarbons,[7,95] the decomposition of formic acid,[69] and other reactions have been included amongst pseudo-homogeneous reactions. The "pseudo-liquid phase" is manifested kinetically by the fact that the rate of the reaction catalysed by the deposited HPA is proportional to the concentration of the active component and not its surface area. Such relations have been found in the study of the conversion of methanol on deposited silver and copper salts of PW_{12}.[97,98] However, in the case of the HPA themselves, the rate, which initially increases with increase of the amount of acid on the carrier, subsequently reaches a plateau; thus the specific catalytic activity calculated per HPA molecule diminishes. This can be explained by the fact that, on increasing the amount of deposited acid, the absorption of the substrate in the bulk of the catalyst becomes the rate-limiting stage of the catalytic process. The latter is analogous to the internal diffusion inhibition in the case of the usual porous catalysts. Another possible explanation is a considerable contribution of the surface reaction.

The correlation of the catalytic activity with the acidity of the massive HPA specimens may serve as evidence for pseudohomogeneity. Thus the rates of the above reactions decrease almost linearly as the H^+ in $H_3[PW_{12}O_{40}]$ is substituted by sodium or pyridine is added, falling almost to zero after the introduction of three pyridine molecules or three sodium ions per PW_{12} anion.[7,69,94,95] In the case of surface reactions, the specific surface of the catalyst plays a decisive role. For example, in the conversion of dimethyl ether into hydrocarbons, the insoluble salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ (specific surface 101 $m^2\ g^{-1}$) shows a higher activity per unit mass of the catalyst than $H_3[PW_{12}O_{40}]$ (specific surface 5 $m^2\ g^{-1}$).[92]

By virtue of the similarity of the properties of crystalline and dissolved HPA, their acidities in the solid state and in solution depend on the composition of the acid in virtually the same way. As a result of this, the rates of pseudohomogeneous reactions catalysed by solid HPA are usually well correlated with the dissociation constants of the acids in solution and with the strengths of the solid acids measured by the method involving the thermal desorption of ammonia or pyridine. Thus the activity of massive HPA in the dehydration of 2-propanol at 100 °C diminishes in the sequence $PW_{12} > SiW_{12} > PW_{10}P_2 > PMo_{12} \approxeq PMo_{10}V_2 \approxeq SiMo_{12}$,[1,5] which is close to the acidity series in solution (Table 2). The lower activity of PMo_{12} compared with SiW_{12} can be explained by the reduction of PMo_{12} during the reaction.[5]

The absorption of 2-propanol in the bulk of the catalyst during dehydration on $H_3[PW_{12}O_{40}]$ has been demonstrated by the rapid replacement of 2-propanol-d_0 in the gas stream by 2-propanol-d_8.[94] In the absence of the catalyst, the d_0 molecules were rapidly (in the course of 2 min) replaced by the d_8 molecules at the outlet from the reactor. In the presence of the catalyst, the exchange took a much longer time (~20 min) which confirms the sorption of the alcohol in the bulk of the HPA. These data made it possible to estimate the amount of alcohol in the catalyst, which was ~7 molecules per anion, corresponding to the coverage of the $H_3[PW_{12}O_{40}]$ surface by approximately 100 alcohol monolayers. This demonstrates convincingly the presence of 2-propanol in the bulk of the catalyst. It has also been found that the rate of absorption is 50 times higher than the rate of dehydration of propanol and absorption does not therefore limit the rate of the catalytic reaction under these conditions (80 °C).

The question of the relative contributions of the bulk and surface reactions to the observed catalytic activity of HPA catalysts naturally arises. It can be answered by comparing the activities of massive specimens of the acids and the dispersed acids on carriers with respect to reactions characterised by pseudo-homogeneity. As already mentioned, in many reactions the catalytic activity of HPA deposited on inert carriers, calculated per acid molecule, is much higher than for massive specimens of the acids. This has been observed both in surface reactions (alkylation of benzene by ethylene,[36] isomerisation of but-1-ene [94]) and in the typical bulk-phase 2-propanol dehydration reaction.[36] The specific catalytic activity is independent of the concentration of deposited HPC only in the conversion of methanol on the silver and copper salts of PW_{12}.[97,98] However, this may be associated with the characteristic features of the formation of the acid centres in the HPA salts (see below). Thus the impression is created that in pseudo-homogeneous reactions the activity of solid HPA catalysts is determined to a larger extent by the degree of dispersion of the acid than by its bulk-phase properties. This may be associated with the difference between the strengths of the surface and bulk-phase protic centres of the HPA (see below) or with the slow course of absorption, as a result of which the reaction proceeds preferentially in the layer near the surface.

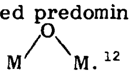
Pseudo-homogeneity apparently plays a significant role in low-temperature reactions of polar substances, i.e. under conditions where the degree of sorption of the substrate in the bulk of the catalyst is high. In high-temperature reactions, the contribution of the bulk-phase reaction is probably not so great. However, the available data are still too few to reach a final conclusion. Detailed kinetic studies of catalysis by deposited HPA are necessary.

The practical value of the phenomenon of the "pseudo-liquid phase" arises because it becomes possible to regulate specifically the selectivity of the catalytic process by differentiating the acid reactions of polar and non-polar substances on coarsely dispersed soluble and finely dispersed insoluble HPC—for example, $H_3[PW_{12}O_{40}]$ and $Cs_{3-x}H_x[PW_{12}O_{40}]$.[55,99] The selectivity can also be altered by employing the difference between the rate of desorption of the intermediates from the surface of the catalyst and from its bulk phase.

An example of such regulation of selectivity is provided by the conversion of dimethyl ether into a mixture of C_1–C_6 alkenes and alkanes on massive PW_{12} HPC at 290 °C.[99] The alkenes are the primary products from which alkanes are formed. The alkene/alkane ratio is clearly correlated with the absorption capacity of the catalyst. Thus, in the case of the acid $H_3[PW_{12}O_{40}]$, which absorbs the ether in an amount corresponding to approximately 40 monolayers (28 °C), the propene/propane ratio is approximately unity. The salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ sorbs less than one monolayer and we have the ratio propane/propane ≈ 12. These data have been explained as follows.[97] The alkenes formed on the surface of the $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ catalyst are readily desorbed. The alkenes obtained in the bulk of the catalyst, namely the acid $H_3[PW_{12}O_{40}]$, its sodium salts, etc. undergo hydrogen transfer reactions with formation of alkanes before being desorbed. Other examples of the regulation of selectivity have been published.[69]

Theoretically the HPA capable of behaving as a "pseudo-liquid phase" are unique objects for the study of one of the main problems of catalysis—the relation between homogeneous and heterogeneous catalysis.

(c) *The acid centres of heteropolyacid catalysts.* As already mentioned, massive HPA exhibit purely Brønsted acidity.[1,5,7] In terms of its strength, they are superior to aluminosilicates[5] and are much more active than the zeolite HY in the dehydration of 2-propanol.[100] It is believed that the protic centres of the HPA are fairly uniform, at least as regards the bases sorbed in the bulk phase (ammonia, pyridine).[93] These conclusions can be extended also to HPA on inert carriers.

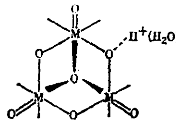
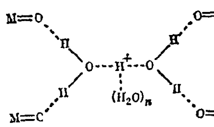
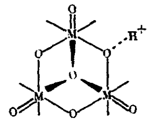
Data on the crystal and proton structures of HPA permit a series of hypotheses about the structure of the acid centres of the catalyst considered. The protons in the free HPA molecules (in solution and probably on the surface of the inert carrier for a low coverage) are localised predominantly at the oxygen atoms of the angular bridges  $M\overset{O}{\diagup\diagdown}M$.[12] In massive acids, the protons participate in the formation of the crystal structure, linking together the HPAN by hydrogen bonds.[12] In the crystals, the positions of the protons may be different because they are determined not only by the negative charge on the oxygen atoms of the polyanion but also by the character of the packing and the unit cell parameters. Indeed, a structural study[34] has shown that the protons in the hexahydrate $H_3[PW_{12}O_{40}]$ enter into the composition of the dioxonium ions $H_2O...H^+...OH_2$, each of which links four neighbouring HPAN by forming hydrogen bonds between the protons of the water molecules and the terminal oxygen atoms of the W=O group. On dehydration, the size of the unit cell diminishes.[14] The exact data concerning the positions of the protons in the dehydrated acids are lacking, but, by analogy with hydrates, one may assume that the crystal structure is determined by the presence of a hydrogen bond between the HPAN via the terminal oxygen atoms, $M{=}O...H^+...O{=}M$, where the non-hydrated proton assumes the role of the binder.

Thus the structure of the Brønsted acid centres in HPA catalysts should depend on their phase state (homogeneous, heterogeneous, massive, or deposited) and the degree of hydration. On the basis of the available structural data, we shall now attempt to represent the structure of the proton centres of the main types of catalysts of this kind (Table 6).

In homogeneous systems the HPA molecules exist in a free state in solution. Their acid centres are homogeneous; they include hydrated (solvated) protons, which are most probably localised at the oxygen atoms of the angular bridges  $M\overset{O}{\diagup\diagdown}M$, linking the metal atoms in the M_3O_{13} triads. The structure of such centres can be represented as structure (I), where three equivalent bridging oxygen atoms in the six-membered metallocycle serve as centres at which the hydrated protons are localised. In the middle of the skeleton of the triad there is an internal oxygen atom through which the triad is linked to the heteroatom.

The heterogeneous catalysts include bulk-phase and surface acid centres. Their structures may be different for the massive and deposited forms. According to some data,[34] the bulk-phase proton centres of the massive hexahydrate of the PW_{12} acid have the structure (II), which incorporates a dioxonium ion linked via hydrogen bonds to the terminal oxygen atoms of the four anions in the unit cell. In highly hydrated acids, the $H_5O_2^+$ ion may be additionally hydrated and the water molecules can also participate in the formation of hydrogen bonds between the anions.[12,34] Such protons centres are apparently responsible for the occurrence of the low-temperature psuedo-homogeneous reactions involving the liberation of water, for example, the dehydration of 2-propanol at 80–150 °C. In vapour-phase reactions at a higher temperature, they are hardly retained as a consequence of the dehydration of the acid.

Table 6. The proton centres of catalysts based on heteropolyacids.

No.	Structure of proton centre*	Type of catalyst	Characteristics of the proton centre
(I)		Homogeneous	Centre in isolated HPA molecule in solution
(II)		Massive heterogeneous	Bulk-phase centre in highly hydrated HPA
(III)	M=O···H⁺···O=M	Massive heterogeneous	Bulk-phase centre in dehydrated HPA
(IV)		Deposited heterogeneous	Centre in highly dispersed acid on a carrier or surface centre in the massive acid

*M = Mo or W.

The bulk-phase centres of the dehydrated HPA can be represented by the structure (III). It is natural to suppose that the structures (II) and (III) can be reversibly interconverted in the course of the acid hydration–dehydration process. The bulk-phase proton centres (III) probably play a significant role in high-temperature pseudo-homogeneous reactions such as the conversion of methanol and dimethyl ether into hydrocarbons at 250–350 °C.

The structural characteristics of the deposited HPA have so far been inadequately investigated. The structure (IV) may be adopted for the proton centres of highly dispersed HPA on the surfaces of inert carriers. It is analogous to the structure of the HPA centres in solution. The difference consists only in the fact that in the deposited catalyst the water content has been reduced to a minimum as a result of heat treatment. If the HPA concentration on the carrier is sufficient for the formation of a two-dimensional or three-dimensional phase, the proton centres of the deposited catalyst may be represented by the set of structures (II)–(IV) depending on the degree of hydration. As regards the surface proton centres of massive HPA, the structure (IV) can be adopted for them although one cannot rule out the additional involvement in the surface reactions of the bulk-phase centres (II) and (III) in the layer near the surface.

The ideas about the structure of the acid centres of the HPA examined may be extended also to acid alkali metal salts.

The question of the realtive activities of different acid centres is very important. Unfortunately, there are as yet insufficient data for a detailed comparison, but certain estimates are possible. It has been found that the activity of the surface acid centres of massive $H_3[PW_{12}O_{40}]$ in the heterogeneous dealkylation of 2,6-di-t-butyl-4-methylphenol in the substrate melt is close to the activity of the centres in the corresponding homogeneous process in solution in acetic acid.[73] This result appears to be entirely natural, since the structures of the centres (I) and (IV) are identical, but it would be too early to treat it as a general rule.

There are not yet any reliable experimental data for the comparison of the activities of the bulk-phase centres (II) and (III), but they can be compared with the centres (IV) in highly dispersed acids on the surface of an inert carrier. As already mentioned, the deposited acids are a little more active than the massive specimens per one acid molecule in typical bulk-phase reactions such as the dehydration of 2-propanol and the esterification of acetic acid by ethanol.[36] This shows that the surface centres (IV) are more active than the bulk-phase centres (II) and (III). This is evidently caused by their different strengths and accessibilities. The more accessible centres (IV), incorporating isolated protons, undoubtedly exhibit a stronger protonating capacity than the centres (II) and (III) in which the protons are bound more strongly, because they participate in the formation of the crystal structure. The surface centres (IV) apparently play the main role in heterogeneous catalysis in many instances.

The structure may be refined and the strength of various proton centres may be estimated in principle by quantum-chemical methods. A semi-empirical calculation has been carried out for the cluster $M_3O_{16}X$ modelling the acid centre (IV), within the framework of the extended Hückel method.[37] The electronic structure of $PMo_{12}O_{40}^{3-}$ has been calculated in terms of the LCAO-MO approximation.[101]

(d) *The formation of acid centres in the salts of heteropolyacids.* Many neutral HPA salts catalyse reactions occurring on Brønsted acid centres and the activity of the salts of certain metals greatly exceeds the activity of the initial acids.[7,64,76,102,103] The neutral salts themselves do not possess an appreciable acidity. This is evident, for example, from the fact that, when pyridine is adsorbed on them, pyridinium ions are not formed and they totally fail to catalyse reactions such as the cracking of cumene and the isomerisation of *o*-xylene, which occur on proton centres, including HPA.[76] It has been established that the salts acquire a strong Brønsted acidity and a high catalytic activity on interaction with the reaction medium. Depending on the nature of the metal cation, one of two mechanisms of the generation of acid centres operates: the hydrolytic[104] or oxidation-reduction[76] mechanisms.

The hydrolytic mechanism is characteristic of metal cations with a high electronegativity (Al^{3+}, La^{3+}, Zn^{2+}, etc.). The Brønsted acid centres are formed as a result of the dissociation of water molecules in the coordination sphere of the metal ion in accordance with the equation

$$M^{n+} + H_2O \rightleftharpoons M(H_2O)^{n+} \rightleftharpoons M(OH)^{(n-1)+} + H^+.$$

The correlation between the catalytic activity and the electronegativity of the metal cation is a sign of the hydrolytic mechanism because the acid dissociation constants of the aquo-complexes are well correlated with the electronegativities.[105] Such correlation has been found in the dehydration of 2-propanol on PMo_{12} salts.[104]

The oxidation-reduction mechanism predominates for salts with metal cations having a fairly high oxidation potential (Ag^+, Cu^{2+}, Pd^{2+}, Pt^{4+}, etc.).[7,76] The acid centres are formed as a result of the reduction of the metal cations by the components of the reaction medium. A typical example is provided by the conversion of methanol into hydrocarbons in the presence of the silver and copper salts of PW_{12}.[7,103] The hydrogen formed as a result of the dehydrogenation of the alcohol then plays the role of the reductant. Traces of H_2 have indeed been detected in the methanol conversion products. The proton centres are formed in accordance with the equations

$$Ag^+ + {}^1/_2H_2 \rightarrow Ag^0 + H^+ ,$$
$$Cu^{2+} + {}^1/_2H_2 \rightarrow Cu^+ + H^+ .$$

The conversion of methanol in the presence of PW_{12} salts has a long induction period, during which the acid centres are produced. When H_2 is introduced into the system, the induction period vanishes. The activity of the salts after treatment with hydrogen at 300 °C exceeds the activity of the initial acid. Small amounts of added O_2 reversibly suppress the catalytic activity of the salt, probably as a result of the reaction:

$$2Ag^0 + 2H + {}^1/_2O_2 \rightarrow 2Ag^+ + H_2O .$$

We may note that, in the hydrolytic formation of acid centres, the catalytic activity of the salts is independent of the presence of H_2 in the system. It is not yet clear why the salts reduced with hydrogen are more active than the initial acids. In our view, this may be accounted for by the activation of the substrate by metal cations or other metal species.

Active catalysts of the conversion of methanol have been prepared by treating with hydrogen the silver salt of PW_{12} deposited on Pd/SiO_2.[66] The mechanism of the formation of the acid catalyst probably involves the dissociation of the hydrogen molecule by metallic palladium. Next, the H atoms, migrating on the surface as a result of spill-over, reduce the silver salt of PW_{12}.

After treatment with hydrogen, the silver and copper salts of PW_{12} catalyse the cracking of cumene and the isomerisation of *o*-xylene.[76] The palladium salt of PW_{12} reduced with hydrogen is an active catalyst of the isomerisation of alkanes.[77] A bifunctional catalyst, incorporating zerovalent palladium and the HPA, is formed in this system via the oxidation-reduction mechanism. The catalytic process involves the dehydrogenation of the alkane on the zerovalent palladium and the subsequent acid skeletal isomerisation. An analogous catalyst has been obtained from a platinum(IV) salt.[66]

(e) *Certain catalytic reactions with participation of heteropolyacids and their salts.* Recently, much attention has been devoted to the synthesis of hydrocarbons from coal in connection with the limited availability of petroleum resources. One of the main aspects of the solution of this problem is the synthesis of hydrocarbons from methanol. Methods have been developed for the conversion of methanol into an artificial liquid fuel containing paraffinic and aromatic hydrocarbons, ranging from C_7 and above, using high-silicon zeolites as catalysts.[106] However, the HPA PW_{12} and SiW_{12} as well as their salts also catalyse the conversion of methanol into hydrocarbons.[2,95,102] A mixture of olefins and alkanes ranging from C_1 to C_7 as well as water and dimethyl ether are formed in the reaction occurring at atmospheric pressure and 250–350°C.

The C_3–C_5 compounds predominate among the hydrocarbons. In contrast to the reaction on zeolites, the yield of compounds above C_7 and aromatic hydrocarbons is very low. This difference is probably due to the molecular sieve effect of zeolites, as a result of which the reaction of hydrocarbons within the zeolite pores is more extensive than on the HPA.

The composition of the products renders HPA unsuitable for the synthesis of motor fuel. However, they are of interest for the selective synthesis from methanol of hydrocarbons such as ethylene and propene. The preferred catalysts for this purpose are the insoluble PW_{12} salts with organic and inorganic cations, which have a large surface area.[99] Vigorous research is being prosecuted on these lines.

The activity of PW_{12} salts in the conversion of methanol decreases in the following sequence (the yields of hydrocarbons, expressed as percentages, at 300 °C are indicated in brackets):[102] Ag(98) > Cu(60) ≅ H(60) > Fe(48) > Al(36) > Pd(26) > La(24) > Zn(13). An analogous series has been obtained for the SiW_{12} salts: Ag(79) > Cu(61) > H(39) > Fe(24) > Al(15) > Zn(7) > La(2). The proportions of different hydrocarbons in the methanol conversion products on HPA and their salts are the same,[102] which indicates that a common mechanism of the catalytic process operates. It has been suggested that the conversion of methanol occurs in the bulk of the catalyst via a carbonium ion mechanism.[2,95]

The alkylation of aromatic compounds by olefins is a large-scale industrial process. Tungsten HPA, which catalyse this reaction, are much more active than the usual heterogeneous catalysts (aluminosilicates, H_3PO_4/SiO_2, etc.). The optimum efficiency in the alkylation of benzene by propene has been achieved when the HPA was used at 150 °C and a pressure of 15 atm, while in the case of the aluminosilicate catalyst the highest efficiency was at 300 °C and 30 atm.[71]

The industrial synthesis of t-butyl methyl ether, an additive which increases the octane number of motor fuel, is carried out by the reaction of isobutene with methanol in the liquid phase in the presence of a cation-exchange resin:[107]

$$(CH_3)_2C{=}CH_2+CH_3OH\rightarrow(CH_3)_3COCH_3\ .$$

HPA catalyse this reaction in both liquid and vapour phases.[63, 108–110] The activity of solid acids in the vapour-phase synthesis of TBME at 90 °C decreases in the sequence $H_3[PW_{12}O_{40}] \cong H_4[SiW_{12}O_{40}] > H_3[PMo_{12}O_{40}] \cong$ zeolite HY > SiO_2–Al_2O_3 > $H_4[SiMo_{12}O_{40}]$. Alumina is completely inactive.[110]

The PW_{12} and SiW_{12} acids and their silver and copper salts, deposited on activated charcoal (30 wt.%), ensure a process selectivity of 100% at 50–110 °C for degrees of conversion of isobutene in the range 30–40%.[64] The activity of the salts increases after treatment with hydrogen. The salt $Ag_3[PW_{12}.O_{40}]$, reduced with hydrogen at 200–300 °C, is more active than $H_3[PW_{12}O_{40}]$. The rate of reaction increases with increase in the concentration of $Ag_3[PW_{12}O_{40}]$ on the carrier to 50 wt.% and then remains constant. The yield of TBME increases with decrease of temperature as a consequence of the displacement of the reaction equilibrium towards the product. At 50 °C and for the volume ratio methanol/isobutene = 1, the yield of TBME on the 30% $Ag_3[PW_{12}O_{40}]/C$ catalyst was 76% for a selectivity of 100%. This catalyst is three times more active than the industrial catalyst (the Amberlite 15 cation-exchange resin)[64] and 100 times more active than aluminosilicates.[5]

Using solid HPA, certain traditional liquid-phase processes can be carried out in the vapour phase. An excellent example is provided by the nitration of benzene. The industrial process involving nitration with a mixture of concentrated nitric and sulphuric acids was developed a very long time ago but hitherto problems of the processing of the acid employed and of the waste water have not been finally solved. In the presence of the $H_3[PW_{12}O_{40}]/SiO_2$ catalyst benzene is nitrated with nitrogen dioxide in the vapour phase at 270 °C.[66] The reaction takes place in accordance with the equation

$$C_6H_6+NO_2\rightarrow C_6H_5NO_2+NO+H_2O\ .$$

Dinitrobenzene is not formed. The rate of the process increases with increase in the $H_3[PW_{12}O_{40}]$ content to 30% and then remains constant. The yield of nitrobenzene, reaching 56%, increases in the presence of water vapour, which probable stabilises the HPA structure.

The number of examples illustrating the high efficiency of HPA catalysts could be greatly increased. In many instances they are more active than the usual acid catalysts and satisfy to a greater extent the energy and ecological requirements which must be met by modern chemical industry.

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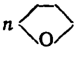
Extensive information about the catalytic properties of HPA has now accumulated. Many new catalytic processes have been developed and some of them have already begun to be used in industry. However, much still remains to be done both as regards the development of the theoretical principles of catalysis by HPA and as regards its practical application.

HPA are extremely interesting as model objects for the study of the elementary steps in heterogeneous acid catalysis. Together with the experimental methods, quantum-chemical calculations in terms of the cluster approximation can be used effectively for this purpose. The behaviour of solid HPA as the "pseudo-liquid phase" leads to unique possibilities for the study of the relation between homogeneous and heterogeneous catalysis.

The synthesis and study of the catalytic properties of new HPC, incorporating different elements as central atoms, ligands, and outer-sphere cations, constitutes an urgent problem. An interesting application of HPC is bifunctional catalysis with simultaneous transfer of protons and electrons, which has so far been little investigated. The employment of HPC as catalysts of a wide variety of processes in fine organic synthesis, including asymmetric synthesis, is promising. Because of the high price of the products, the gain in selectivity in this instance as a result of the introduction of the more effective catalyst frequently greatly exceeds the expenditure on the catalyst.

During the preparation of the review for the press, the VIIIth Japanese–Soviet Seminar on Catalysis, "Catalysis by New Materials", was held in Tokyo. Studies on catalysis by HPA, including the practical utilisation of these catalysts, were widely represented.[111–116] At the present time, tungsten HPA are used in Japan in the industrial manufacture of 2-propanol, 2-butanol, and t-butyl alcohol by the liquid-phase hydration of the corresponding olefins. A process leading to the polymerisation of tetrahydrofuran in the presence of $H_3PW_{12}O_{40}$ has been developed:[115]

n  $+ H_2O \rightarrow HO{-}[{-}(CH_2)_4{-}O{-}]_n{-}H$.

The construction of a factory in Japan for the application of this process is being completed.

The vapour-phase oxidation of methacrolein to methacrylic acid in the presence of a heterogeneous catalyst based on PMo_{12} is used on a large scale (80 000 tonnes annually).[111] Thus the industrial application of HPA catalysts abroad is increasing at a high rate, which confirms the urgent need to develop this field in our country.

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Organic Compounds of Polyvalent Iodine-Derivatives of Iodosobenzene

E.B.Merkushev (deceased)

The review describes the latest advances in the chemistry of aliphatic and aromatic iodoso-compounds, iodosohalides, iodosocarboxylates, and the derivatives of μ-oxobisacyloxy(aryl)iodine. A separate section is devoted to polymers with tervalent iodine.

The bibliography includes 300 references.

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I. INTRODUCTION

Having passed chlorine through a solution of iodobenzene in chloroform in 1886, Willgerodt[1,2] obtained, instead of the expected substitution product, the addition product $PhICl_2$, which was called phenyl iodosochloride in accordance with one of the then current nomenclatures. During the period which has elapsed since then, a wide variety of organic compounds containing iodine in the tervalent or quinquevalent state have been synthesised and their chemical properties have been investigated.

During the 1950's–1960's extensive studies were carried out on iodonium salts by Beringer in the USA and Nesmeyanov, Vanags, and Neilands in the USSR. Since the 1970's, the chemistry of aryl iodosocarboxylates has been developing successfully as a result of the efforts of scientists from many countries.

Despite the fact that the number of publications on the chemistry of organic compounds of polyvalent iodine is relatively small, nevertheless they have been covered in chronological order by fairly large numbers of periodically published reviews. The studies up to 1914 have been described in Willgerodt's monograph,[3] those published up to 1942 are dealt with in Sandin's review[2] already mentioned, and the studies up to 1965 are surveyed in Banks's review.[4] The data on all organic compounds of polyvalent iodine known up to 1955 are presented in the form of Tables in the review by Beringer and Gindler.[5] At the present time this field of chemistry has developed so widely that it is not possible to describe its present state in a single journal publication. There exists a brief review on iodonium salts[6] and one of the chapters of a monograph[7] is devoted to organic compounds of polyvalent iodine—mainly iodonium salts. The chemistry of aryl iodosocarboxylates is dealt with in a recently published review[8] and their application as oxidants is described in a monograph.[9] A review[10] is devoted to the use of polyvalent iodine compounds (mainly organic compounds) in organic chemistry. Interesting data on the chemistry of iodonium salts can be found also in other communications[11,12] and information about the chemistry of aryl iodosocarboxylates is available in books.[13,14]

The majority of organic compounds of polyvalent iodine belong to one of three large groups: the iodonium salts $R_2I^+X^-$, the iodonium ylides $R-\overset{+}{I}-\overset{-}{E}$ ($E = C$ or N), and derivatives of iodosobenzene PIY_2 ($Y_2 = O$ or $Y = Cl$, F, or RCO_2).† The present review is devoted to the last group of compounds. The relation between various organic compounds of polyvalent iodine is illustrated in Scheme 1 for phenyl derivatives.

II. IODOSO-COMPOUNDS

1. Synthesis

Usually only the iodoso-derivatives of aromatic and heteroaromatic compounds and to a lesser extent vinyliodoso-compounds are relatively stable.[2] Among derivatives containing an iodine atom linked to an *sp*^{3}-carbon atom, only perfluoroalkyliodoso-derivatives are stable.

The iodoso-group can be introduced into certain arenes with electron-accepting substituents using the reaction of the latter with iodosyl sulphate:[16,17]

$$ArH \xrightarrow{(IO)_2SO_4/H_2SO_4} ArIO$$

Among the methods based on the hydrolysis of phenyl iodosochloride or phenyl iodosoacetate,[18,19] preference should be given to the latter because it is less laborious and the initial compound is stable on storage. Iodosobenzene can be prepared by the reaction of phenyl iodosochloride with silver oxalate, carbonate, or nitrate in acetonitrile.[20]

A number of specific methods for the synthesis of perfluoroalkyliodoso-derivatives have been proposed—for example the ozonolysis of perfluoroiodoalkanes,[21] the hydrolysis of the trifluoroacetates of iodosoperfluoroalkanes,[22] or

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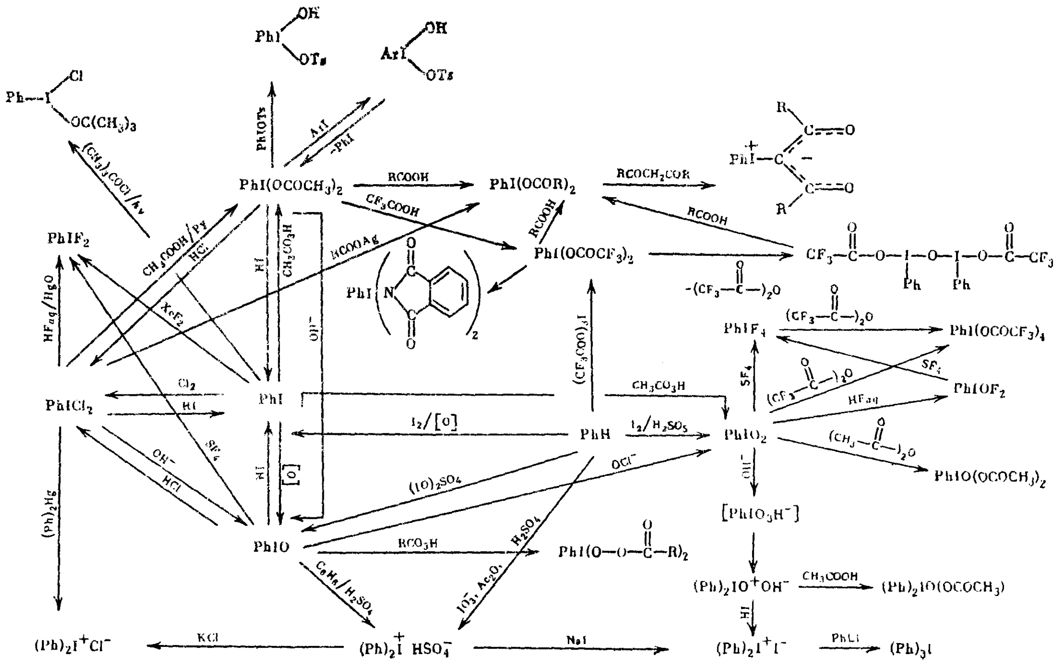
†The existence of iodosobenzene in the polymeric form $(PhIO)_n$ has been reported.[15]

Scheme 1



the interaction of perfluoroalkyl iodosofluorides with silicon dioxide.[21]

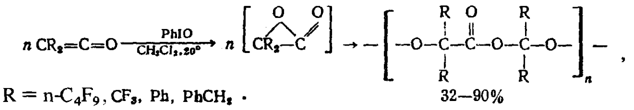
The stability of the iodoso-compounds of all classes is low; they disproportionate on storage:[4,21]

$$2R{-}IO \rightarrow R{-}I + R{-}IO_2\ ,$$
$$R = Ar,\ C_nF_{2n-1}\ .$$

2. Properties

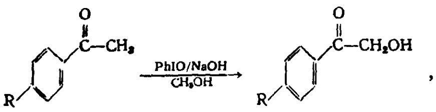
Iodoso-compounds have been used mainly as oxidants. Scant information about the early studies may be found in reviews.[2,4] A number of new reactions involving oxidation by iodosobenzene have been described in a series of communications.[23–25]

Fruitful researches into the oxidation of compounds of a wide variety of classes by iodosobenzene in an alkaline medium were initiated in the 1980's. Ketens give rise to unstable α-lactones, which polymerise at the instant of formation:[26]



R = n-C_4F_9, CF_3, Ph, $PhCH_2$. 32—90%

Acetophenones (I) are oxidised to ω-hydroxyacetophenones (II):[27]

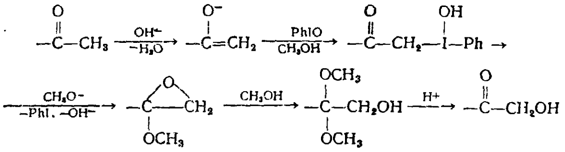


(I) (II), 45—71%

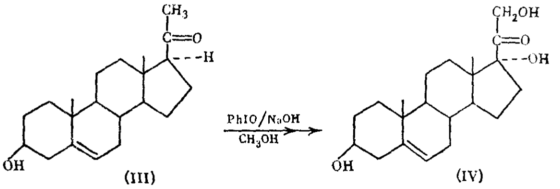
R=H, CH_3, OCH_3, F, Cl, Br, I, NO_2 .

2,6-Diacetylpyridine is oxidised by phenyl iodosoacetate (PIA) in an alkaline medium to 2,6-di(hydroxyacetyl)pyridine in 63% yield.[27]

The acetyl group can be converted to the hydroxy-acetyl group via the following scheme:[28,29]



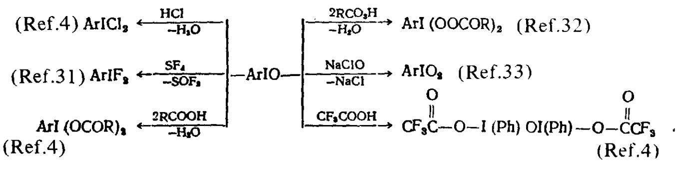
The reaction discovered made it possible to transform the steriod derivative (III) into the derivative (IV) with a high yield:[29,30]



(III) (IV)

Iodosobenzene converts tetracyanoethylene into the corresponding epoxide in 74% yield.[26]

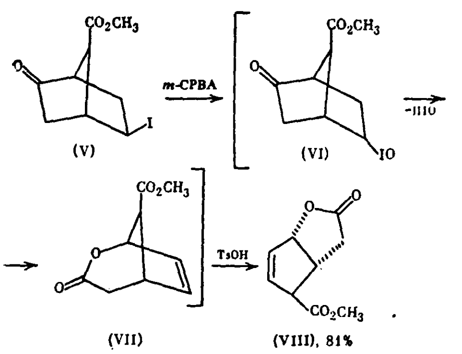
Iodosoarenes can be readily converted into organic compounds of polyvalent iodine belonging to different classes:[4,31–33]



(a) Oxidation Reactions of Alkyl Iodides#, §

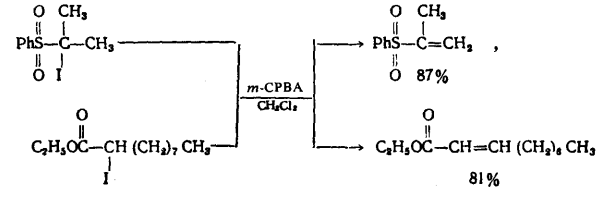
Alkyl iodides are resistant to the action of $KMnO_4$, H_2O_2, or O_3 but under the influence of certain oxidants, usually peracids, they are converted into esters or ethers, vicinal diesters, α-iodoesters, alcohols, ketones, or oxirans.[37–40] The mechanisms of these reactions have not so far been ultimately elucidated but the intermediate formation of aliphatic iodoso-derivatives is usually postulated.

The reaction involving the conversion of the bicyclic iodide (V) under the influence of *m*-chloroperbenzoic acid (m-CPBA) to the lactone (VIII) was described in 1977. The lactone is probably formed via the iodoso-derivative (VI) which is converted into the unsaturated bicyclic lactone (VII) by splitting off HIO:[41]

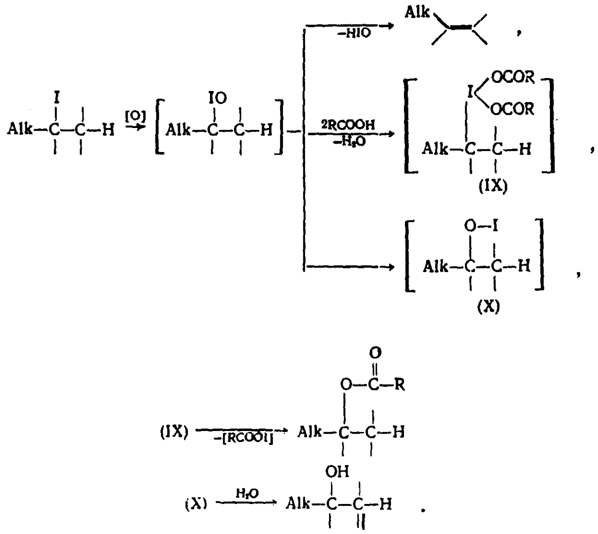


(V) (VI) (VII) (VIII), 81%

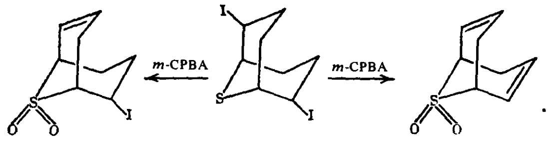
Many details of the reaction of alkyl iodides with peracid were elucidated by Reich and Peake.[42] In a neutral medium, primary alkyl iodides are oxidised by *m*-CPBA to alcohols with a satisfactory yield. Alkyl iodides having electron-accepting groups in the α-position converted into alkenes:



In all cases the initial oxidation products are iodoso-compounds whose subsequent fate depends on the structure of the alkyl iodide. The iodoso-compound can split off hypoiodous acid (*syn*-elimination) or can react with the organic acid to form the iodosocarboxylate (IX), which is not isolated and is converted further into an ester. A rearrangement of the iodoso-compound via a radical or ion pair into the alkyl hypoiodite (X) with subsequent hydrolysis to an alcohol is also possible:

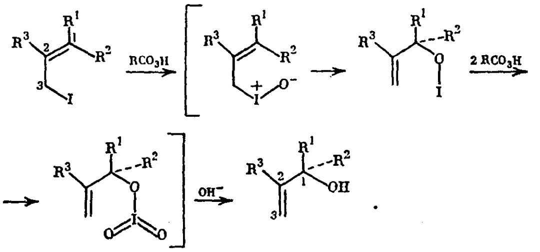


On oxidation with *m*-CPBA, the bicyclic sulphide (XI) gives rise to the unsaturated sulphones (XII) or (XIII) depending on the reaction conditions:[43]

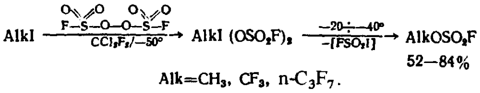


(XII), 62% (XI) (XIII), 70%

Allyl iodides are oxidised by peracids to allyl alcohol via the intermediate formation of derivatives of tervalent and quinquevalent iodine {the reaction involves a [2,3]sigmatropic rearrangement}:[44]



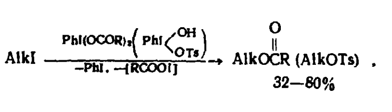
Alkyl iodides are converted into alkyl fluorosulphates under the influence of peroxydisulphuryl difluoride:[45]



$$AlkI \xrightarrow[CCl_2F_2/-50^\circ]{F-SO_2-O-O-SO_2-F} AlkI(OSO_2F)_2 \xrightarrow[-[FSO_2I]]{-20 \div -40^\circ} \underset{52-84\%}{AlkOSO_2F} ;$$

$$Alk=CH_3,\ CF_3,\ n\text{-}C_3F_7.$$

The reactions of alkyl iodide with phenyl iodosocarboxylates or phenyl iodosohydroxytosylate lead to esters:[46,47]



$$AlkI \xrightarrow[-PhI,\ -[RCOOI]]{PhI(OCOR)_2\left(PhI\begin{smallmatrix}OH\\OTs\end{smallmatrix}\right)} \underset{32-80\%}{AlkOC(=O)R\ (AlkOTs)} .$$

Esters are also formed when alkyl iodides are oxidised by derivatives of μ-oxobisacyloxy(aryl)iodine.[33,47]

#See Zefirov and co-workers.[34–36]

§In certain studies such reactions are referred to by the term "oxidative deiodination". It cannot be regarded as apt since the reaction RI → RH is usually associated with the term "deiodination". It is probably better to call these reactions "oxidative substitution of an iodine atom".

When alkyl iodides are oxidised with iodine pentafluoride, aldehydes are produced,[48] oxidation with phenyl iodosochloride affords alkyl chlorides,[1] and oxidation with iodine tris(trifluoroacetate) gives rise to alkyl trifluoroacetates.[49]

Alkenes interact with iodine trichloride to form 1,2-dichloroalkanes, which are probably formed via unstable alkyl iodosochlorides.[50]

The oxidation of alkyl iodides in the presence of salts of acids whose anions are superweak nucleophiles leads to the replacement of iodine by the anion of these acids. The reaction described probably proceeds via a stage involving the formation of carbonium ion intermediates:[51,52]

$$\mathrm{CH_3(CH_2)_nI} \xrightarrow[\mathrm{CH_2Cl_2,\ -78\div+50^\circ}]{[\text{oxidant}]/\mathrm{M^+OR^-}} \underset{20\text{—}70\%}{\mathrm{CH_3(CH_2)_nOR}}\ ;$$

$\mathrm{R{=}CH_3,\ CF_3,\ }p\text{-}\mathrm{CH_3C_6H_4}.$

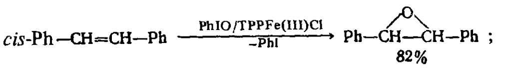
It is at present difficult to estimate the synthetic value of reactions involving the oxidative substitution of the iodine atom in alkyl iodides, because many communications are only preliminary and do not give experimental details. However, the value of such reactions is apparently very high; for example, the reaction of methylene iodide with nitronium fluoroborate in the presence of tetrabutylammonium perchlorate results in the formation of methylene bisperchlorate, otherwise difficult to obtain, in nearly quantitative yield.[34]

For the biological oxidation of alkyl halides, including alkyl iodides, see Macdonald et al.[53]

(b) Catalytic Oxidation¶

There exists a large group of oxidation reactions in which iodosobenzene is smoothly involved only in the presence of various metal-containing catalysts.

The ability of iodosobenzene to hydroxylate organic compounds in the presence of cytochrome P-450 has been demonstrated.[55,56] Various metal-containing porphyrins are simple models of the active centre of cytochrome P-450. The ease of oxygen transfer from iodosobenzene to organic substrates in the presence of porphyrins containing iron, chromium, or manganese has been demonstrated.[57-61] It is difficult to predict whether these reactions will find applications in preparative organic chemistry, because studies carried out hitherto have been devoted mainly to the elucidation of the mechanism of the enzyme action. However, many reactions take place extremely stereoselectively; for example *cis*-stilbene is epoxidised in a high yield, while the *trans*-isomer is almost inert:



$$cis\text{-}\mathrm{Ph{-}CH{=}CH{-}Ph} \xrightarrow[\mathrm{-PhI}]{\mathrm{PhIO/TPPFe(III)Cl}} \underset{82\%}{\mathrm{Ph{-}\overset{\frown O\frown}{CH{-}CH}{-}Ph}}\ ;$$

TPPFe(III)Cl = chloro(5,10,15,20-tetraphenylprophyrinato)iron.

There is apparently no need to use the fairly complex catalysts mentioned above. The ability of iodosobenzene to oxidise readily alcohols to aldehydes and ketones and disubstituted alkynes to α-dicarbonyl compounds at room temperature in methylenechloride in the presence of $\mathrm{RuCl_2{-}P(Ph)_3}$ has been demonstrated.[62-64]

In the presence of iron-containing porphyrins, iodosobenzene oxidises sulphides to sulphoxides.[65,66] Certain sulphoxides can be oxidised by this system to the corresponding sulphones.

III. IODOSOHALIDES

1. Iodosochlorides

(a) Synthesis

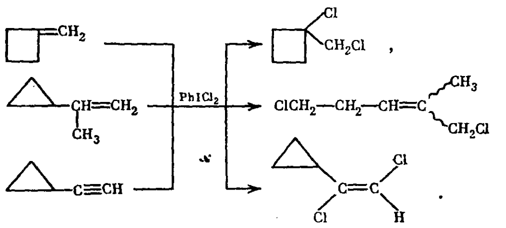
On treatment with chlorine in a solvent, aryl iodides give rise to aryl iodosochlorides.[4] Vinyl iodides are also capable of forming vinyl iodosochlorides. For example, *trans*-diiodoethylene is converted into *trans*-iodovinyl iodosochloride.[67] *trans*-Chlorovinyl iodosochloride can be obtained in a high yield from acetylene.[67-69]

Aliphatic iodosochlorides are as a rule unstable and can be obtained only at low temperatures.[67] The iodosochlorides derived from alkyl iodomethyl sulphones proved to be unexpectedly stable.[70,71]

(b) Chlorination

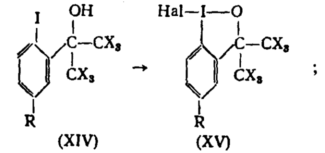
Aryl iodosochlorides are mild chlorinating agents and in solution are able to chlorinate alkenes on thermal or photochemical initiation with formation of vicinal chloride. The reaction mechanism is complex. The reaction can proceed via both radical and ionic mechanisms.[72,73] When alkanes are chlorinated, the tertiary carbon atom is attacked preferentially.[74]

Unsaturated hydrocarbons with cycloalkyl substituents produce high yields of dichlorides.[75,76] It is of interest to note that the trimethylene ring is attacked preferentially in 2-cyclopropylpropene:



Steroid derivatives are also chlorinated by phenyl iodosochloride.[77-79] It has been shown that there is a possibility of the selective halogenation of steroid alcohols with subsequent introduction of a double bond using iodosochlorides based on carboxylic acids having the general formula $\mathrm{Cl_2I.(C_6H_4)_nCOOH}$ (n = 0–4), joined to the steroid molecules by ester linkages.[80] The reaction of ethers with phenyl iodosochloride affords the α-chloro-derivatives, while molecular chlorine usually leads to αα′-dichloro-derivatives.[81] Molecular chlorine converts diazoketones into resins, but phenyl iodosochlorine produces geminal dichlorides.[82] The use of phenyl iodosochloride for the chlorination of triphenylphosphine-acylmethylenes has been described.[83,84]

The iodine-containing alcohols (XIV) have been converted into halogeno-iodinanes (XV),[85] which are convenient reagents for benzyl and allyl halogenation:[85]



(XIV) (XV)

R=H, CH₃; X=H, F; Hal=Br, Cl, F .

Numerous studies have been made of the influence of polar effects on radical chlorination by aryl iodosochlorides,[86-95] but unfortunately much still remains obscure in this problem.

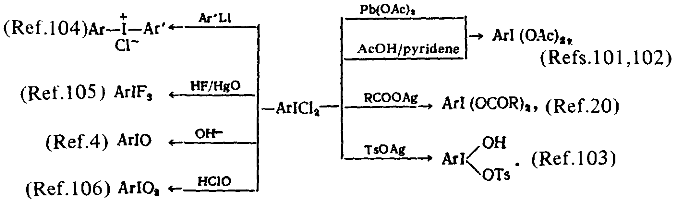
¶For a brief review, see Meunier.[54]

(c) Oxidation

Phenyl iodosochloride in aqueous pyridine converts sulphides and selenides into sulphoxides and selenoxides.[96,97] Phenyl diphenylmethyl sulphide is cleaved by phenyl iodosochloride to benzenesulphenyl chloride and diphenylmethyl chloride.[98] Secondary steroid alcohols are converted into the corresponding ketones in good yields on treatment with the phenyl iodosochloride–pyridine system.[99] The iodosochloride based on 3-iodopyridine is capable of oxidising selectively secondary alcoholic groups in steroid polyalcohols.[100]

(d) Different Reactions

Like iodoso-compounds, aryl iodosochlorides are widely used in the synthesis of various derivatives of polyvalent iodine:[4,20,101–106]

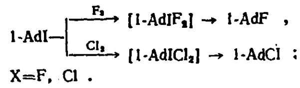


Aryl iodosochlorides are unstable substances which decompose on storage.[4] The main product of the decomposition of phenyl iodosochloride is *p*-chloroiodobenzene.[107]

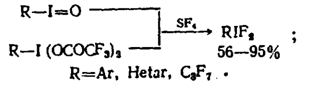
2. Iodosofluorides

(a) Synthesis

They can be obtained from derivatives of univalent or tervalent iodine. Iodosofluorides can be synthesised by fluorinating iodides with elemental fluorine,[108] chlorine trifluoride,[109,110] or xenon difluoride.[111,112] On treatment with molecular fluorine or chlorine, 1-iodoadamantane is converted into 1-fluoro or 1-chloroadamantane via the intermediate formation of iodosohalides, which are not isolated:[113]



Phenyl iodosofluoride was obtained in a high yield by the electrolysis of silver fluorine in acetonitrile in the presence of iodobenzene.[114] Aryl iodosofluorides can be prepared by condensing iodoso-compounds with 48% hydrofluoric acid[115–117] or by treating iodosochlorides with hydrogen fluoride in the presence of mercury(II) oxide.[105] Iodosofluorides can be synthesised most conveniently by the interaction of iodoso-compounds or iodosotrifluoroacetates with sulphur tetrafluoride:[22]

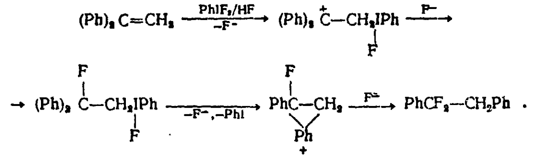


(b) Fluorination

The reaction of 1,1-diphenylethylene with phenyl iodosofluoride affords 1,1-difluoro-1,2-diphenylethane.[105] 3,3-Diphenylprop-2-ene behaves analogously:[118,119]

$$(Ph)_2C{=}CH{-}CH_3 \xrightarrow[CHCl_3,\ -20°]{PhIF_2} PhCF_2{-}CH(Ph){-}CH_3 \ .$$

These reactions probably proceed via a stage involving the formation of a phenonium ion:[120]



Ketones are fluorinated by phenyl iodosofluoride in the α-position.[121] The fluorination of compounds of different classes by methyl iodosofluoride and aryl iodosofluorides has been investigated in a number of studies.[122–125]

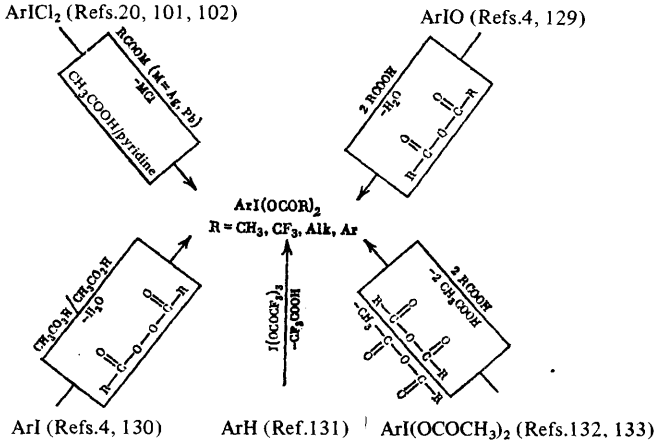
IV. IODOSOCARBOXYLATES

While the nomenclature† of iodonium salts is identical in different countries, the nomenclature of organic compounds of quinquevalent iodine is still in a state of constant development; one would think therefore that the time had come to adopt an unambiguous nomenclature for aryl iodosocarboxylates. For example, more than a dozen different names may be found in the chemical literature of different countries during the last 25 years for the compound $PhI(OCOCH_3)_2$, first synthesised by Willgerodt and called by him phenyl iodoacetate ("Phenyliodacetat").[3] Aryl iodosocarboxylates can probably be named as iodosoesters—derivatives of hydrated iodosoarenes $ArI(OH)_2$, i.e. the compound $PhI.(OCOCF_3)_2$ can be called phenyl iodosotrifluoroacetate, while in the case of partial esters the prefix "hydroxy" is used, for example, the compound PhI(OH)Ts would be called phenyl iodosohydroxytosylate.[127] In the case of mixed iodosoesters, the acid residues forming part of their composition are named alphabetically, i.e. the compound $PhI.(OCOCH_2Br)(OCOCH_2Cl)$ is called phenyliodosobromoacetate-chloroacetate.[128]

1. Synthesis

The scheme presented below illustrates different methods of synthesis of aryl iodosocarboxylates:

Scheme 2



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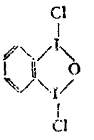
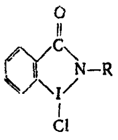
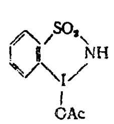
†For the IUPAC recommendations concerning the nomenclature of organic compounds of polyvalent iodine, see Ref.126.

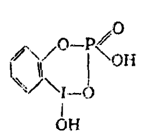
The reaction of arenes with iodine tris(trifluoroacetate) in trifluoroacetic acid or methylene chloride leads to aryl iodosotrifluoroacetates.[131]

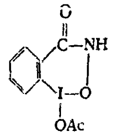
The oxidation of *o*-substituted aryl iodides sometimes leads to the formation of heterocyclic compounds containing tervalent iodine in the ring, for example compounds (XVI)–(XX):[134–139]


(XVI)


(XVII)


(XVIII)


(XIX)


(XX)

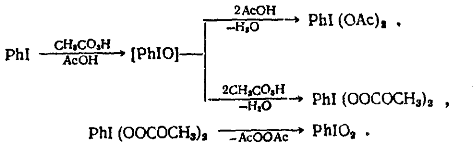
R=CH_3, CH_2CH_2Cl, $CH_2CO_2CH_3$.

It is of interest to note that phenyl iodoso-*p*-nitrophenylbenzoate is formed on decomposition of *p*-nitrophenylbenzoyl peroxide in iodobenzene.[130] Although this reaction takes place at high temperatures, where aryl iodosocarboxylates usually decompose, it is apparently pssible to select mild conditions for the decomposition of acyl peroxides, whereupon these reactions can become a good preparative method of synthesis of aryl iodosocarboxylates.

Phenyl iodosochloride reacts with lead diacetate or silver salts of carboxylic acids to form phenyl iodosocarboxylates in high yields.[20,101] Aryl iodosochlorides with electron-donating substituents give rise to aryl iodosoacetates on treatment with acetic acid in the presence of pyridine.[102]

The condensation of iodoso-compounds with carboxylic acids also leads to aryl iodosocarboxylates.[4] This reaction is complicated by the instability and poor solubility of iodoso-compounds in the usual organic solvents; it is normally carried out in liquid carboxylic acids, whose excess serves as the solvent (the attempts to condense iodosobenzene with solid carboxylic acids in organic solvents were unsuccessful[140,141]). In these reactions the carboxylic acids can be successfully replaced by their anhydrides.[129,142,143]

The availability of aryl iodosoacetates, their stability on storage, and their ready solubility have made these compounds key reagents in the synthesis of various aryl iodosocarboxylates. Aryl iodosoacetates can be prepared in high yields by oxidising aryl iodides with 30% H_2O_2 in acetic anhydride[144] or with 40% peracetic acid and acetic acid.[145] When iodobenzene is oxidised with the latter reagent, iodoxybenzene may be formed.[146] The mechanism of this process is not entirely clear; iodoxybenzene may be formed on decomposition of the peroxy-compound arising as a result of the condensation of iodosobenzene with peracetic acid:[147]



The exchange reaction of aryl iodosoacetates with substituted benzoic acids can serve as a preparative method of synthesis of the corresponding benzoates.[148,149] Phenyl iodosocarboxylates can be obtained by the exchange reaction between the phenyl iodoso-trifluoroacetate (PITFA) and the sodium salts of carboxylic acid in acetonitrile.[150]

When the exchange reaction between aryl iodosoacetates or aryl iodosotrifluoroacetates and carboxylic acids was carried out in high-boiling solvents at a reduced pressure, it became a universal procedure, which permitted the synthesis of a large series of iodosocarboxylates containing the residues of aliphatic, aromatic, and heterocyclic acids as well as the residues of acylated aminoacids[132] (Table 1):

$$PhI(OAc)_2 \xrightarrow[-2AcOH]{2RCOOH/C_6H_4Cl} PhI(OCOR)_2 .$$

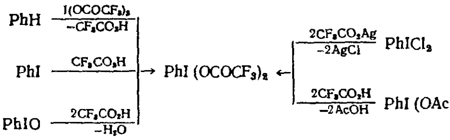
Table 1. Phenyl iodosocarboxylates $PhI(OCOR)_2$.[132]

R	Yield, %	R	Yield, %
Ethyl	72	*o*-Iodophenyl	32
Propyl	81	*o*-Phenylphenyl*	96
Isopropyl	82	*p*-Methoxyphenyl*	83
t-Butyl	82	*p*-Nitrophenyl	96
Diphenylmethyl	85	3,5-Dinitrophenyl	98
Fluoromethyl	91	*o*-Acetoxyphenyl**	62
Chloromethyl	94	*o*-(2-Formylphenyl)phenyl**	58
Trichloromethyl	82	4-Fluorenonyl**	98
2,4-Dichlorophenoxymethyl	92	2-Furyl	60
Phenyl	96	*N*-Benzoylglycyl	92
o-Bromophenyl	66	*N*-Benzoyl-DL-alanyl	96

*The solvent used for the exchange reaction was o-dichlorobenzene.

**Solvent–nitrobenzene.

The methods of synthesis of two phenyl iodosocarboxylates, namely $PhI(OCOCF_3)_2$ and PhI(OH)OTs, which have become in recent years multipurpose reagents for organic synthesis, merit special consideration. Phenyl iodosotrifluoroacetate can be prepared from benzene, iodobenzene, phenyl iodosochloride, and phenyl iodosoacetate (PIA):[4,20,131,132,151]



The best of these methods involves the exchange reaction of phenyl iodosoacetate with trifluoroacetic acid. It occurs on simple recrystallisation of PIA from warm (but not boiling) trifluoroacetic acid.[132,151]

Phenyl iodosohydroxytosylate (PIHT) can be prepared by condensing silver tosylate with phenyl iodosochloride or by the exchange reaction of toluene-*p*-sulphonic acid with phenyl iodosoacetate.[103,127] The latter method is more convenient.

2. Oxidation Reactions

All the numerous reactions of aryl iodosocarboxylates with organic compounds can be divided into two large groups. The first group embraces reactions during which aryl iodosocarboxylates are reduced to iodoarenes and various oxidation products not containing iodine are formed from organic substrates. Reactions during which aryl iodosocarboxylates are not reduced and the compounds formed contain a tervalent iodine atom may be assigned to the second group.

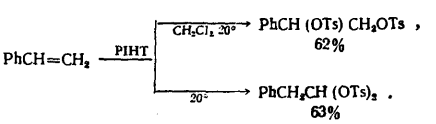
Almost all the oxidation reactions in the first group can be subdivided into three subgroups. The first includes reactions of aryl iodosocarboxylates with various acids (OH, NH, and SH- etc. acids). Reactions of aryl iodosocarboxylates with unsaturated compounds, usually leading to acyloxylation products, belong to the second sub-group. The third subgroup comprises the oxidation reactions of compounds containing heteroatoms (S, P, Se) with formation of the corresponding oxides.

The reactions of the second group are subdivided into two subgroups: the formation of iodonium salts and iodonium ylides.

(a) Alkenes

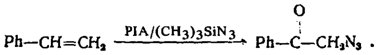
When alkenes react with PIA, PITFA, or PIHT, vicinal diesters are formed.[140,152–154]

On treatment with PIHT, styrene is converted either into 1-phenyl-1,2-di(tosyloxy)ethane or into 2-phenyl-1,1-di(tosyloxy)ethane depending on the reaction conditions:[154]



$$\mathrm{PhCH{=}CH_2} \xrightarrow{\text{PIHT}} \begin{cases} \xrightarrow{\mathrm{CH_2Cl_2},\ 20^\circ} \mathrm{PhCH(OTs)CH_2OTs}\ , & 62\% \\ \xrightarrow{20^\circ} \mathrm{PhCH_2CH(OTs)_2}\ . & 63\% \end{cases}$$

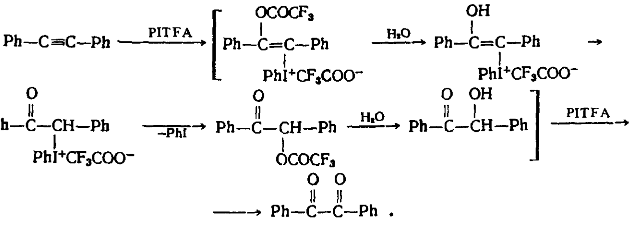
Propene reacts with the PIA/I_2 system to form 2-acetoxy-1-iodopropane in a high yield.[24] The reaction of this system with keten leads to the mixed anhydride of acetic and iodoacetic acids, which can be converted into iodoacetic acid or its anhydride.[155] On treatment with the PIA/$(CH_2)_3SiN_3$ system, styrene is converted into an azide:[156]



$$\mathrm{Ph{-}CH{=}CH_2 \xrightarrow{PIA/(CH_3)_3SiN_3} Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_2N_3}\ .$$

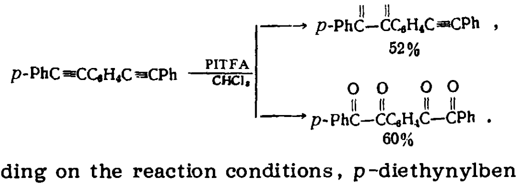
(b) Alkynes

Diarylacetylenes are inert when acted upon by both PIA and lead tetraacetate.[157] However, PITFA oxidises tolanes with electron-donating and not very strong electron-accepting substituents in moist chloroform to the corresponding benzils in good yields.[158] The reaction probably proceeds with the intermediate formation of vinyl- and alkyl-iodonium salts:[158]



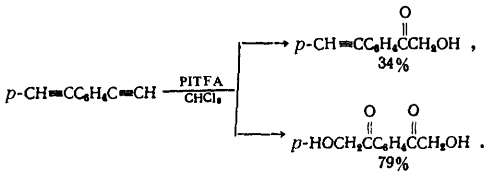
$$\mathrm{Ph{-}C{\equiv}C{-}Ph \xrightarrow{PITFA} \left[Ph{-}\overset{OCOCF_3}{\overset{|}{C}}{=}\underset{\underset{PhI^+CF_3COO^-}{|}}{C}{-}Ph \xrightarrow{H_2O} Ph{-}\overset{OH}{\overset{|}{C}}{=}\underset{\underset{PhI^+CF_3COO^-}{|}}{C}{-}Ph \rightarrow Ph{-}\overset{O}{\overset{\|}{C}}{-}\underset{\underset{PhI^+CF_3COO^-}{|}}{CH}{-}Ph \xrightarrow{-PhI} Ph{-}\overset{O}{\overset{\|}{C}}{-}\underset{\underset{OCOCF_3}{|}}{CH}{-}Ph \xrightarrow{H_2O} Ph{-}\overset{O}{\overset{\|}{C}}{-}\overset{OH}{\overset{|}{CH}}{-}Ph \right] \xrightarrow{PITFA} Ph{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}Ph}\ .$$

We have shown that PITFA oxidises 1,4-di(phenylethynyl)benzene to 4-phenylglyoxaloyltolane or to 1,4-di(phenylglyoxaloyl)benzene:[159]



$$p\text{-}\mathrm{PhC{\equiv}CC_6H_4C{\equiv}CPh} \xrightarrow[\mathrm{CHCl_3}]{\text{PITFA}} \begin{cases} p\text{-}\mathrm{Ph\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}C_6H_4C{\equiv}CPh}\ , & 52\% \\ p\text{-}\mathrm{Ph\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}Ph}\ . & 60\% \end{cases}$$

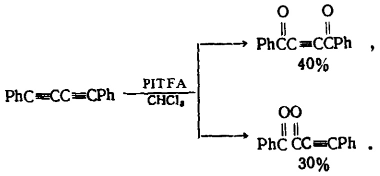
Depending on the reaction conditions, *p*-diethynylbenzene is converted into 1-ethynyl-4-hydroxyacetylbenzene or into 1,4-di(hydroxyacetyl)benzene:[160]



$$p\text{-}\mathrm{CH{\equiv}CC_6H_4C{\equiv}CH} \xrightarrow[\mathrm{CHCl_3}]{\text{PITFA}} \begin{cases} p\text{-}\mathrm{CH{\equiv}CC_6H_4\overset{O}{\overset{\|}{C}}CH_2OH}\ , & 34\% \\ p\text{-}\mathrm{HOCH_2\overset{O}{\overset{\|}{C}}C_6H_4\overset{O}{\overset{\|}{C}}CH_2OH}\ . & 79\% \end{cases}$$

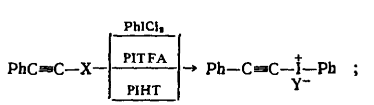
It must be emphasised that at present PITFA is the only reagent capable of oxidising selectively one triple bond in the molecules of polyacetylenic compounds.

Diphenylbutadiyne is oxidised by PITFA to a mixture of dibenzoylacetylene and phenyl(phenylglyoxaloyl)acetylene:[161]



$$\mathrm{PhC{\equiv}CC{\equiv}CPh} \xrightarrow[\mathrm{CHCl_3}]{\text{PITFA}} \begin{cases} \mathrm{Ph\overset{O}{\overset{\|}{C}}C{\equiv}C\overset{O}{\overset{\|}{C}}Ph}\ , & 40\% \\ \mathrm{Ph\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}C{\equiv}CPh}\ . & 30\% \end{cases}$$

Phenylacetylene reacts with phenyl iodosochloride, PITFA, or PIHT to form acetylenic iodonium salts:[159,162,163]



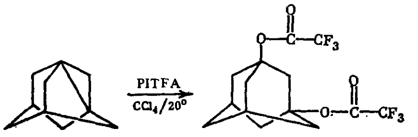
$$\mathrm{PhC{\equiv}C{-}X} \xrightarrow{\mathrm{PhICl_2}\ /\ \text{PITFA}\ /\ \text{PIHT}} \mathrm{Ph{-}C{\equiv}C{-}\overset{+}{I}{-}Ph\ ;}\quad \mathrm{Y^-}$$

X=Li, Y=Cl; X=H, Y=CF_3CO_2; X=H, Y=TsO .

The stability of such salts increases with decrease of the nucleophilicity of the anion. Disubstituted acetylenes react with the PIA/I_2 system to form *trans*-β-acetoxy-α-iodoalkenes, which readily hydrolyse to α-hydroxyketones.[164]

(c) Cyclopropanes

Various cyclopropylphenyl iodosoacetates were synthesised for the first time in 1979.[165] The three-membered ring in phenylcyclopropane is opened by PITFA with formation of 1-phenyl-1,3-bis(trifluoroacetoxy)propanes.[166] The same reaction takes place also with PIA in a chloroform–trifluoroacetic acid mixture, in which PITFA is formed *in situ*.[167] The strained 1,3-dehydroadamantane (XXI) interacts with PITFA to form the unstrained 1,3-bis-(trifluoroacetoxy)-adamantane (XXII) in a high yield:[168]



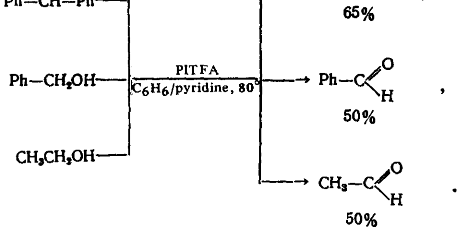
(XXI) (XXII)

(d) Polynuclear Condensed Hydrocarbons

9,10-Dihydroanthracene is dehydrogenated by PITFA or phenyl iodosophthalimidate to anthracene.[151,169] PITFA can oxidise anthracene further to a mixture of 1,2- and 9,10-anthraquinones.[170]

(e) Alcohols, Glycols, Phenols, and Hydroperoxides

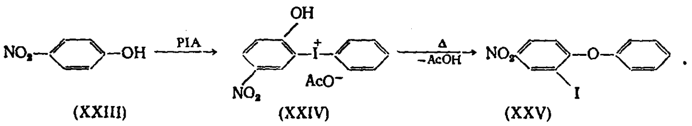
Alcohols of different classes react with PIA or PITFA, being oxidised to carbonyl compounds:[4,151]



$$\left.\begin{matrix} \mathrm{Ph{-}\overset{OH}{\overset{|}{C}H}{-}Ph} \\ \mathrm{Ph{-}CH_2OH} \\ \mathrm{CH_3CH_2OH} \end{matrix}\right\} \xrightarrow[\mathrm{C_6H_6/pyridine},\ 80^\circ]{\text{PITFA}} \begin{cases} \mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}Ph}\ , & 65\% \\ \mathrm{Ph{-}CHO}\ , & 50\% \\ \mathrm{CH_3{-}CHO}\ . & 50\% \end{cases}$$

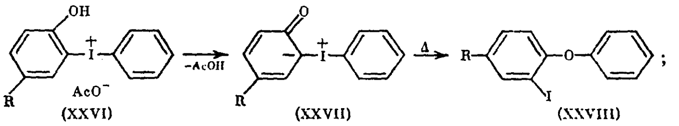
Phenyl iodosoacetate oxidises alcohols in the form of halogenomagnesium alkoxides generated *in situ* from the alcohols and n-propylmagnesium bromide.[171]

The reaction involving the oxidation of phenols by PIA yields a complex mixture of products, in which quinones and o-acetoxyphenols predominate.[172] 4-Nitrophenol (XXIII) is converted into 2-hydroxy-5-nitrodiphenyliodonium acetate (XXIV), which can rearrange on heating via a reaction having an unknown mechanism into 2-iodo-4-nitrophenyl phenyl ether (XXV):[148]



(XXIII) (XXIV) (XXV)

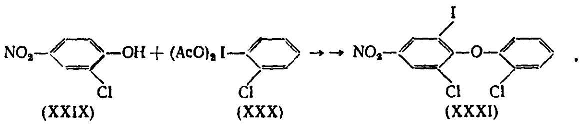
The oxidation of p-ethoxycarbonyl-, p-formyl-, or p-acetylphenols proceeds analogously. The iodonium salts (XXVI), formed initially, split off an acetic acid molecule and are converted into the iodonium ylides (XXVII), which can rearrange to the diphenyl ethers (XXVIII):[173]



(XXVI) (XXVII) (XXVIII)

R = NO_2, $COOC_2H_5$, CHO, $COCH_3$.

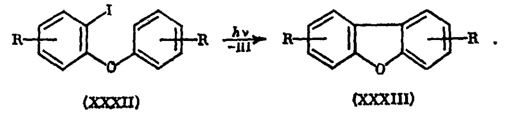
2-Chloro-4-nitrophenol (XXIX) is oxidised by 2-chlorophenyl iodosoacetate (XXX), forming 2-chlorophenyl 2-chloro-6-iodo-4-nitrophenyl ether (XXXI):[174]


(XXIX) (XXX) (XXXI)

However, 2,6-dichloro-4-nitrophenol is oxidised by PIA to 2,6-dichloro-1,4-benzoquinone.[148]

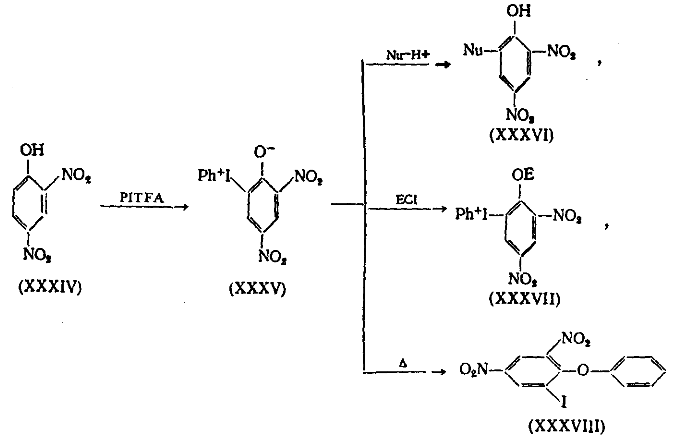
The facts presented permit the conclusion that this interesting reaction is probably general among phenols having an electron-accepting group in the p-position and at least one free o-position.

Photochemical syntheses based on 2-iodo-substituted diphenyl ethers (XXXII) lead to a simple way of preparing substituted dibenzofurans (XXXIII) (see, for example, Kappe et al.[175]):



(XXXII) (XXXIII)

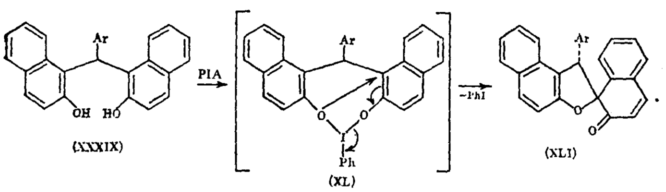
2,4-Dinitrophenol (XXXIV) is oxidised by PITFA to the iodonium salt (XXXV); the latter can react with both nucleophiles and electrophiles, forming the products (XXXVI) and (XXXVII); on heating, compound (XXXV) rearranges to 6-iodo-2,4-dinitrophenyl phenyl ether (XXXVIII):[176]



(XXXIV) (XXXV) (XXXVI) (XXXVII) (XXXVIII)

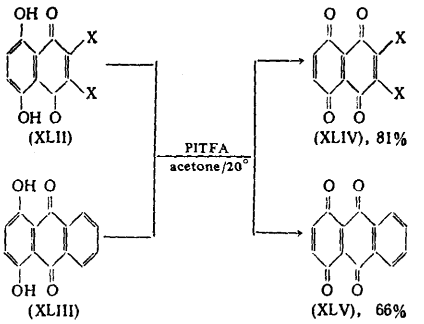
Nu=OH, OCH_3, n-C_4H_9NH; E=H, PCl_2, $Si(CH_3)_3$.

The bisnaphthols (XXXIX) rearrange under the influence of PIA into the spiro-compounds (XLI) via the iodosoethers (XL):[177,178]



(XXXIX) (XL) (XLI)

The reaction of catechol with PIA affords o-benzoquinone in 90% yield.[179] PITFA oxidises 2,3-dichloro-5,6-dicyanohydroquinone to 2,3-dichloro-5,6-dicyanoquinone in 90% yield.[151] PITFA converts the anhydride of hydroquinone-2,3-dicarboxylic acid quantitatively into the anhydride of p-benzoquinone-2,3-dicarboxylic acid.[180] The oxidation of the dihydroxyquinones (XLII) and (XLIII), derived from naphthalene and anthracene, by treatment with PITFA results in the formation of the corresponding diquinones (XLIV) and (XLV):[181]



(XLII) (XLIII) (XLIV), 81% (XLV), 66%

X=H, Cl .

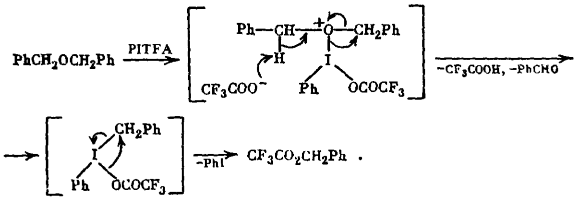
t-Butyl hydroperoxide interacts with PIA at a low temperature to form a new peroxide, which decomposes on raising the temperature:[182]

$$PhI(OAc)_2 \xrightarrow[-2AcOH]{2\ t\text{-}BuOOH} [PhI(OOBu\text{-}t)_2] \rightarrow PhI + O_2 + (t\text{-}BuO)_2 .$$

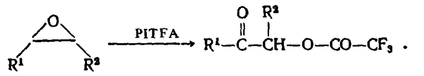
(f) Ethers

On treatment with PITFA, alkyl aryl ethers are converted into iodonium salts.[183] Benzyl ethers are cleaved by PITFA to carbonyl compounds and benzyl or alkyl trifluoroacetate.

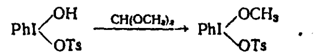
This reaction proceeds via the intermediate formation of an oxonium complex, which is converted, with formation of a carbonyl compound, into a tervalent iodine derivative, which then decomposes to iodobenzene and trifluoroacetate:[184]



Oxirans are converted by PITFA into the trifluoroacetate of α-hydroxyketones:[185]



On reaction with trimethyl orthoformate, PIHT is converted into phenyl iodosomethoxytosylate:[186]

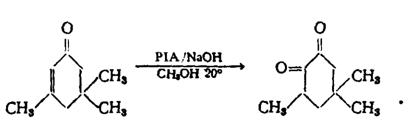


(g) Aldehydes and Ketones

After prolonged contact with PITFA, benzaldehyde is oxidised to benzoic acid. This reaction probably proceeds via the intermediate formation of the mixed anhydride of benzoic and trifluoroacetic acids.[187]

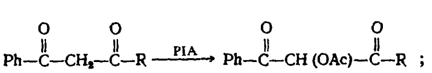
Cyclohexanone reacts with PIA to form 2-hydroxycyclohexanone in 80% yield.[26]

On treatment with PIA, isophorone (XLVI) is converted into 3,5,5-trimethylcyclohexane-1,2-dione (XLVII):[26]



(XLVI) (XLVII)

The reaction of acetophenones with PIA in the presence of sulphuric acid leads to products of the acetoxylation of the methyl group.[188] Benzil is cleaved by PITFA to benzoic acid. This reaction probably also takes place via a stage involving the formation of the mixed anhydride of benzoic and trifluoroacetic acids.[160] Dibenzoylmethane and 4,4,4-trifluoro-1-phenylbutane-1,3-dione are acetoxylated on treatment with PIA:[188,189]

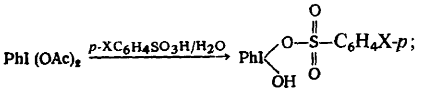


$R=Ph, CF_3$.

Polycarbonyl compounds are cleaved by PIA to carboxylic acids in aqueous acetic acid.[190]

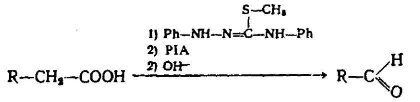
(h) Carboxylic Acids and Water

Aryl iodosocarboxylates enter into exchange reactions with carboxylic acids.[4] The reactions of PIA with substituted benzenesulphonic acid lead to the corresponding phenyl iodosohydroxybenzenesulphonates:[127]



$X=H, CH_3, Cl, NO_2$.

Carboxylic acids having the methylene group in the α-position react with S-methyl-1,4-diphenylisothiosemicarbazide, forming the salts of 5-substituted 3-methylthio-1,4-diphenyl-1,2,4-triazoles. The latter are acetoxylated by PIA at the methylene group and the hydrolysis of the resulting derivative affords aldehydes containing one carbon atom less than the initial acid:[191,192]



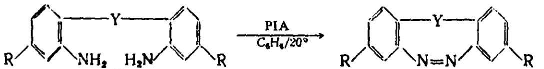
$R=CH_3, C_2H_5, n\text{-}C_7H_{15}$.

The hydrolysis of PIA is the best preparative method of synthesis of iodosobenzene.[19] This reaction proceeds via hydrated iodosobenzene, which loses a water molecule. Under the usual conditions, the reaction requires alkaline catalysts but at elevated temperatures it can take place even under the influence of the traces of moisture present in the solvent (see, for example, Hey et al.[193]).

(i) Primary Aromatic Amines

These are oxidised by aryl iodosocarboxylates to azo-compounds under mild conditions with yields ranging from low to excellent. The reaction takes place via a free-radical mechanism.[194–196]

The amino-derivatives (XLVIII) cyclise under the influence of PIA to diazepines (XLIX):[197,199]

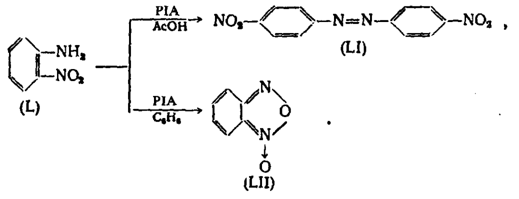


(XLVIII) (XLIX), 35–71%

$Y=CH_2, SO_2$; $R=H, Cl$.

The remarkable reaction involving the oxidation of 4-iodoaniline to 4,4′-diiodoazobenzene by chlorine or peracetic acid can be explained by the intermediate formation of iodosochlorides and iodosoacetates.[199,200]

o-Nitroaniline (L) can be oxidised both to 4,4′-dinitroazobenzene (LI) and to benzofuroxan (LII):[196]

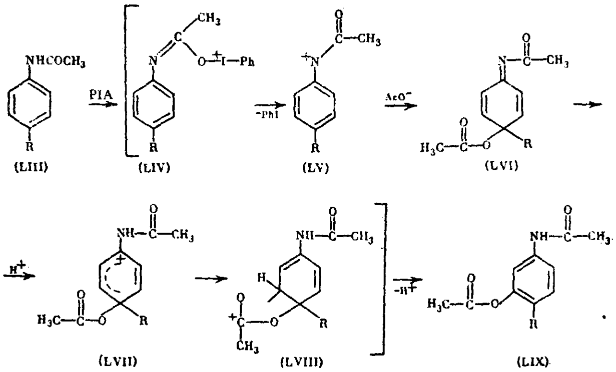


(L) (LI) (LII)

2-Amino-3-nitrobiphenylene is converted into the corresponding furoxan in 70% yield.[201] The oxidative cyclisation reaction is common to anilines having in the o-position a substituent capable of forming a heterocyclic ring.[202]

The reactions of the acetanilides (LIII), having electron-donating groups in the 4-position, with PIA proceed in accordance with the heterocyclic mechanism via the iodonium salt (LIV), the nitrenium cation (LV), and the dienoneimine (LVI).

The protonated form of the latter (LVII) rearranges intramolecularly via compound (LVIII) to the 3-acetoxy-derivative (LIX):[203]

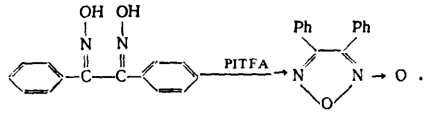


(j) Carboxylic Acid Amides

On reaction with aryl iodosocarboxylates, they are decarbonylated.[204–206] PITFA is a convenient reagent for the stepwise degradation of peptides attached to an insoluble polymeric support.[207]

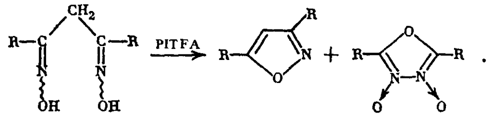
(k) Oximes

α-Dioximes react with PITFA to form mixtures of aldazine di-*N*-oxides and nitrile oxides. The benzil dioxime (LX) is converted into the corresponding furoxan (LXI):[151]



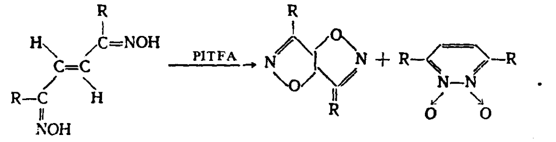
(LX) (LXI), 91%

The β-dioximes (LVII) give rise to mixtures of isoxazoles (LXIII) and 4-oxa-4*H*-pyrazole di-*N*-oxides (LXIV):[208,209]



(LXII) (LXIII) (LXIV)

trans-2-Unsaturated 1,4-dioximes (LXV) react with PITFA to form a mixture of 3a,6a-dihydroisoxazolo[5,4-*d*]isoxazoles (LXVI) and pyridazine 1,2-dioxides (LXVII):[210]



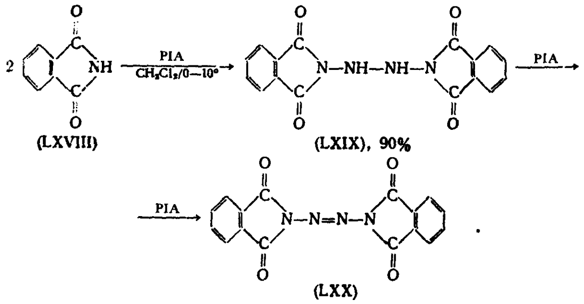
(LXV) (LXVI) (LXVII)

(l) Various Nitrogen-containing Compounds

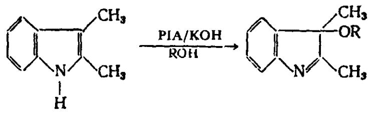
Hydrazobenzene is dehydrogenated quantitatively by PIA to azobenzene.[194] PITFA converts diethyl hydrazodicarboxylate into diethyl azodicarboxylate;[151] PIA is ineffective in this reaction.

Schiff bases are oxidised by PIA with formation of aldehydes and azo-compounds.[211] The interaction of *NN*-dibenzylhydroxylamines with PIA leads to nitrones.[212]

Phthalimide (LXVIII) is oxidised by PIA to the tetrazane (LXIX), which can be converted further into the tetrazene (LXX):[213]



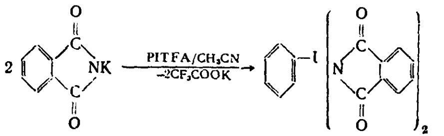
4-Amino-3,5-diphenyl-1,2,4-triazole reacts with PIA to form benzonitrile; in the presence of alkenes, this reaction can lead to aziridines.[214] The reactions of PIA with aryldiazomethanes or 1-aryl-1-diazoethanes affords complex mixtures of products, the main components of which are the trifluoroacetates $ArCH_2OCOCF_3$ or $ArCH(CH_3)OCOCF_3$.[215] On treatment with PIA in the presence of alkali in alcohols, 2,3-dimethylindole (LXXI) gives rise to 3-alkoxyindolenine (LXXII):[216]



(LXXI) (LXXII)

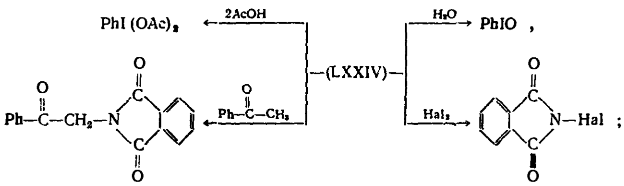
R=CH_3, C_2H_5 .

Phenyl iodosophthalimidate (LXXIV) is obtained by the reaction of potassium phthalimide (LXXIII) with PITFA:[169]



(LXXIII) (LXXIV), 74%

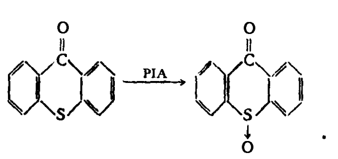
Compound (LXXIV) enters into a series of reactions:[169]



Hal=I, Br .

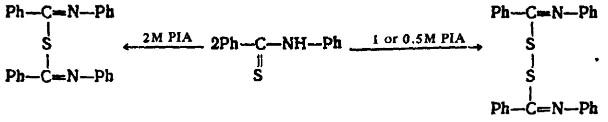
(m) Sulphur-containing Compounds

Thiophenols are oxidised to disulphides on treatment with both PIA [217] and PITFA.[151] The oxidation of sulphides by PIA leads to sulphoxides.[218,219] When the thiaxanthone (LXXV) is treated with PIA, it is converted into the corresponding sulphoxide (LXXVI) in a high yield:[220]



(LXXV) (LXXVI)

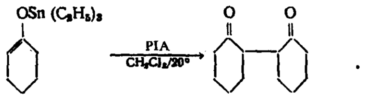
It is of interest to note that phenyl trityl and benzyl trityl sulphides are not oxidised by PIA to the corresponding sulphoxides but are cleaved with formation of diphenylmethanol and probably compounds containing bivalent sulphur.[221] The oxidative elimination of sulphur from various sulphur-containing compounds is possible. On treatment with PIA, thiobenzanilide is converted into benzanilide in aqueous ether.[222] Depending on the reaction conditions, in absolute ether thiobenzanilide is converted into di(α-phenyliminobenzyl) sulphide or into di(α-phenyliminobenzyl) disulphide:[222]



(n) Compounds Containing Phosphorus, Selenium, Boron, and Tin

The reaction of triphenylphosphine with PITFA leads to triphenylphosphine oxide.[8] Selenazines react with PIA to form the corresponding selenazine oxides.[223]

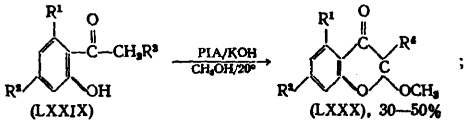
Phenyl iodosoacetate is capable of oxidising boron compounds.[224,225] The triethylstannyl enolate of cyclohexanone (LXXVII) is converted on treatment with PIA into 2,2′-dioxo-1,1′-bicyclohexyl (LXXVIII):[226]



(LXXVII) (LXXVIII), 61%

(o) Polyfunctional Compounds

The reaction of benzoin with PITFA results in the formation of benzil in a high yield.[158] The interaction of *o*-hydroxyacetophenones (LXXIX) with PIA in the presence of KOH affords coumaran-3-ones (LXXX):[227]

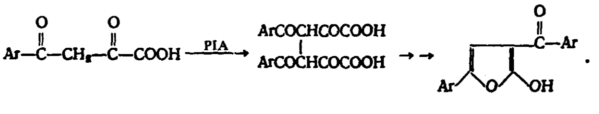


(LXXIX) (LXXX), 30–50%

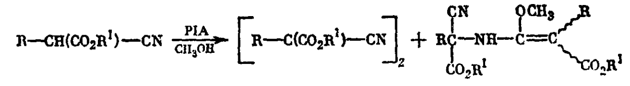
$R^1=R^2=R^3=H$, $R^4=OCH_3$; $R^1=R^2=H$, $R^3=R^4=CH_3$; $R^1=R^2=CH_3$, $R^3=H$, $R^4=OCH_3$; $R^1=R^2=H$, $R^3=R^4=PhCH_2$.

The oxidation of 3-cyanopyrrolidine-2,5-diones with PIA leads to the formation of ring opening products.[228] *NN*-Dialkyl-2-aminoalcohols are cleaved by PIA to aldehydes and iminium salts; the latter hydrolyse to amines and formaldehyde.[229] On treatment with PIA or iodosobenzene, α-ketoacids are decarbonylated.[26,140,230]

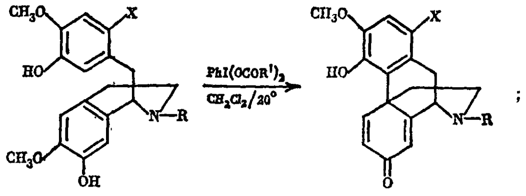
α-Hydroxyacid esters are oxidised by PIA to α-ketoacid esters.[231] 4-Aryl-2,4-dioxobutanoic acids are cyclised by PIA to 4-aroyl-2-aryl-5-hydroxyfurans:[232]



When α-cyanocarboxylates are treated with PIA, they dimerise:[233]



Reticuline (LXXXI) is cyclised by phenyl iodosocarboxylates to salutaridine (LXXXII):[133]



(LXXXI) (LXXXII), 14-32%

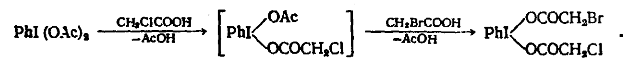
X=H, Br, Cl; R=CH$_3$, CHO, CO$_2$C$_2$H$_5$; R^1=CH$_3$, CCl$_3$, CF$_3$.

The PIA/cyanamide system converts the penicilloic acid derivative (LXXXIII) into the derivative (LXXXIV):[234]

(LXXXIII) (LXXXIV)

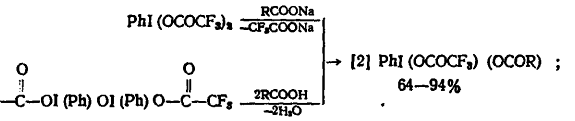
(p) Mixed Iodosocarboxylates

For a long time, the sole representative of these compounds was phenyl iodosobromoacetate-chloroacetate synthesised from PIA:[128]



$$PhI(OAc)_2 \xrightarrow[-AcOH]{CH_2ClCOOH} \left[PhI\begin{matrix}OAc\\OCOCH_2Cl\end{matrix}\right] \xrightarrow[-AcOH]{CH_2BrCOOH} PhI\begin{matrix}OCOCH_2Br\\OCOCH_2Cl\end{matrix}.$$

Iodosocarboxylates contain the residues of various acids, one of which is trifluoroacetic acid, and can be conveniently obtained from PITFA[150] or from μ-oxobis(trifluoroacetoxy)(phenyl)iodine:[33]



$$PhI(OCOCF_3)_2 \xrightarrow[-CF_3COONa]{RCOONa} [2]\ PhI(OCOCF_3)(OCOR);\ 64–94\%$$

$$CF_3\overset{O}{\overset{\|}{C}}-OI(Ph)OI(Ph)O-\overset{O}{\overset{\|}{C}}-CF_3 \xrightarrow[-2H_2O]{2RCOOH} [2]\ PhI(OCOCF_3)(OCOR)$$

R=CH$_3$, CH$_2$Cl, CHCl$_2$.

Cyclohexene reacts with phenyl iodosoacetate-trifluoroacetate to form 1-acetoxy-2-trifluoroacetoxycyclohexane, which readily hydrolyses to 2-acetoxycyclohexanol.[150]

(r) Catalytic Oxidation

Like iodosobenzene, aryl iodosocarboxylates are able to hydroxylate organic compounds in the presence of cytochrome P-450.[235] Tolan is oxidised by the PIA/RuCl$_2$–P(Ph)$_3$ system to benzil[63] and 1-octanol is oxidised to 1-octanal.[62] PIA in aqueous acetic acid containing RuCl$_3$ cleaves fumaric, maleic, arylic, and cinnamic acid as well as styrene at the carbon–carbon double bonds.[236] It has recently been possible to isolate the complex formed in the reaction of PIA with the manganese-containing porphyrin: PhI(OAc)–O–Mn(IV)–O–I(OAc)Ph. This complex hydroxylates organic compounds.[237]

3. Direct Halogenation of Aromatic and Heteroaromatic Compounds

The possibility, in principle, of iodinating *m*-xylene in warm acetic acid by the I_2/PIA or I_2/PhIO system was demonstrated in 1963.[238] Azobenzene is iodinated by the I_2/PIA system in boiling acetic acid, forming 4-iodoazobenzene in a low yield.[239] These iodinating systems have not found extensive application in synthetic organic chemistry. The observation of a fairly unexpected iodination of iodobenzene to *p*-diiodobenzene in a high yield by the I_2/PITFA system in carbon tetrachloride at room temperature[160] led the authors[170,240,241] to investigate the preparative possibilities of this reaction.

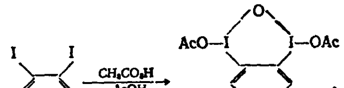
The iodination takes place readily at room temperature when equimolar amounts of PITFA and iodine are mixed with the organic substrate in methylene chloride, chloroform, carbon tetrachloride, or 1,2-dichloroethane:

$$\text{R—H} \xrightarrow[\text{–PhI, –CF}_3\text{COOH}]{\text{I}_2\text{/PITFA}} \text{R—I} \; ; \quad \text{R=Ar, Hetar} \; .$$

This system iodinates compounds which are more reactive in electrophilic substitution reactions than iodobenzene. There is no need to employ PITFA which is unstable on storage—it can be generated in situ from PIA and trifluoroacetic acid.[170] This method is effective for the direct iodination of arylcyclopropanes.[242] The Br_2/PITFA system is convenient for bromination of arenes,[243,244] while the $AlCl_3$/PITFA system is convenient for chlorination.[244] Because of its experimental simplicity, the possibility of carrying out the halogenation at room temperature, and the ease with which the target products can be isolated, the above halogenation method can find extensive application in fine organic synthesis. Certain data on these processes are presented in Table 2.

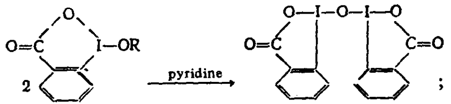
V. DERIVATIVES OF µ-OXOBISACYLOXY(ARYL)IODINE

Although these compounds have been known for a long time, it is noteworthy that until recently there was no convenient method of their synthesis. The oxidation of *o*-diiodobenzene (LXXXV) with peracetic acid yields the µ-oxo-compound (LXXXVI):[134]



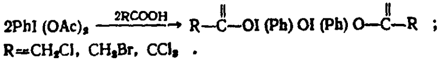
(LXXXV) (LXXXVI)

On treatment with pyridine, derivatives of *o*-iodosobenzoic acid (LXXXVII) give rise to the µ-oxo-compound (LXXXVIII):[141]



(LXXXVII) (LXXXVIII)
R=CH_3, Ac .

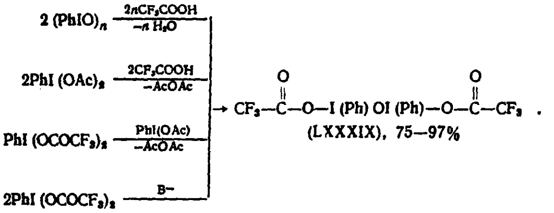
µ-Oxo-compounds can be obtained from PIA:[245]



$$2\text{PhI(OAc)}_2 \xrightarrow{2\text{RCOOH}} \text{R—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—OI(Ph)OI(Ph)O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—R} \; ;$$

R=CH_2Cl, CH_2Br, CCl_3 .

A series of effective approaches to the synthesis of µ-oxobis(trifluoroacetoxy)(phenyl)iodine (LXXXIX) have been proposed:[33]



$$\left.\begin{array}{l} 2\,(\text{PhIO})_n \xrightarrow[-n\,\text{H}_2\text{O}]{2n\text{CF}_3\text{COOH}} \\ 2\text{PhI(OAc)}_2 \xrightarrow[-\text{AcOAc}]{2\text{CF}_3\text{COOH}} \\ \text{PhI(OCOCF}_3)_2 \xrightarrow[-\text{AcOAc}]{\text{PhI(OAc)}} \\ 2\text{PhI(OCOCF}_3)_2 \xrightarrow{\text{B}^-} \end{array}\right| \rightarrow \text{CF}_3\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—O—I(Ph)OI(Ph)—O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—CF}_3 \; .$$

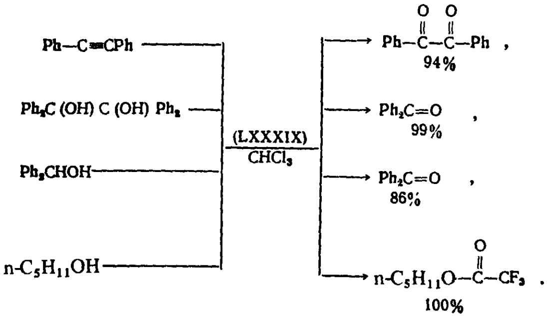
(LXXXIX), 75—97%

Table 2. The synthesis of halogeno-derivatives by halogenation in the presence of PITFA.

Organic substrate	Halogeno-derivative	Yield, %	Refs.
Benzene*	iodobenzene	72	[170]
o-Xylene	4,5-diiodo-*o*-xylene	55	[240]
m-Xylene	4,6-diiodo-*m* xylene	77	[240]
p-Xylene	2,5-diiodo-*p*-xylene	65	[240]
Mesitylene	triiodomesitylene	84	[240]
Durene	diiododurene	52	[240]
Phenylcyclopropane	4-iodophenylcyclopropane	42	[242]
Biphenyl	4,4-diiodobiphenyl	87	[240]
p-Terphenyl	4,4′-diiodo-*p*-terphenyl	93	[170]
Diphenylmethane	4,4′-diiododiphenylmethane	50	[170]
Chlorobenzene*	4-chloroiodobenzene	61	[240]
Bromobenzene*	4-bromoiodobenzene	63	[240]
Iodobenzene*	1,4-diiodobenzene	73	[240]
Diphenyl ether	di(4-iodophenyl) ether	79	[240]
Fluorenone	2,7-diiodofluorenone	51	[240]
Biphenyl-4-carboxylic acid	4-iodobiphenyl-4′-carboxylic acid	81	[170]
Fluorene-9-carboxylic acid	2,7-diiodofluorene-9-carboxylic acid	70	[240]
Methyl fluorene-9-carboxylate	methyl 2,7-diiodofluorene-9-carboxylate	52	[240]
Diphenylene oxide	2,7-diiododiphenylene oxide	59	[170]
o-Carbaborane	9-iodo-*o*-carbaborane	72	[241]
o-Carbaborane	9,12-diiodo-*o*-carbaborane	74	[241]
m-Carbaborane	9-iodo-*m*-carbaborane	64	[241]
Benzene*	bromobenzene	99	[243]
Mesitylene	tribromomesitylene	82	[243]
Biphenyl	4,4′-dibromobiphenyl	96	[243]
Diphenyl ether	di(40bromophenyl) ether	80	[243]
Fluorenone	2,7-dibromofluorenone	73	[244]
4-Methoxybenzoic acid	3-bromo-4-methoxybenzoic acid	81	[244]
Benzene*	chlorobenzene	80	[244]
Mesitylene	trichloromesitylene	63	[244]
Durene	dichlorodurene	38	[244]
Fluorenone	2,7-dichlorofluorenone	93	[244]

*The reaction was carried out in an excess of the aromatic substrate.

Certain data on the oxidative properties of the compounds obtained are illustrated by the equations presented below:[33]

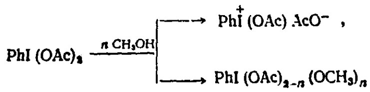


$$\left.\begin{array}{l} \text{Ph—C}\equiv\text{CPh} \\ \text{Ph}_2\text{C(OH)C(OH)Ph}_2 \\ \text{Ph}_2\text{CHOH} \\ n\text{-C}_5\text{H}_{11}\text{OH} \end{array}\right| \xrightarrow[\text{CHCl}_3]{\text{(LXXXIX)}} \left|\begin{array}{l} \rightarrow \text{Ph—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—Ph}\,,\ 94\% \\ \rightarrow \text{Ph}_2\text{C=O}\,,\ 99\% \\ \rightarrow \text{Ph}_2\text{C=O}\,,\ 86\% \\ \rightarrow n\text{-C}_5\text{H}_{11}\text{O—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—CF}_3\,.\ 100\% \end{array}\right.$$

On treatment with like carboxylic acids, the μ-oxo-compounds are converted into phenyl iodosocarboxylates, while unlike carboxylic acids convert them into mixed iodosoesters.[245] Treatment of alkenes with the μ-oxo-compounds results in the formation of vicinal diesters.[246]

VI. SPECTROSCOPIC DATA

X-Ray diffraction data have been obtained for phenyl iodosochloride,[247] PIA,[248] phenyl iodosodichloroacetate,[249] μ-oxobis(trifluoroacetoxy)(aryl)iodine,[33] and 1-hydroxy-3-oxo-3*H*-benzoiodoxole (the cyclic form of *o*-iodosobenzoic acid).[250] ^1H, ^{13}C, and ^{19}F NMR data have been published for various organic compounds of polyvalent iodine;[31,33,136,251,252] the ^{19}F NMR spectra of perfluoroalkyliodoso-compounds have been discussed.[21,253] The observed splitting of the PIA signal in the ^1H NMR spectrum on reducing the temperature in solution in methanol has been interpreted as evidence for the existence of the ionic and covalent forms of PIA at a low temperature.[254] However, it has been shown[233] that PIA interacts with methanol even at very low temperatures and thus the problem has remained open:

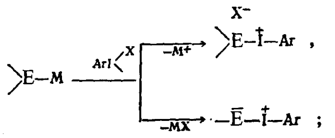


$$PhI(OAc)_2 \xrightarrow{n\,CH_3OH} \begin{cases} Ph\overset{+}{I}(OAc)\,AcO^- , \\ PhI(OAc)_{2-n}(OCH_3)_n . \end{cases}$$

The IR spectra of various polyvalent iodine compounds have been discussed in a series of studies[141,255–257] and the IR and Raman spectra have been described.[15] For data on the dipole moments of aryl iodosocarboxylates, see Exner and Plesnicar.[258] The results of conductimetric studies of solutions of phenyl iodosochloride have been published by Zappi and Cortelezzi[259] and those for PIA solutions can be found in the paper of Johnson and co-workers.[260,261] Erlich and Kaplan[262]# published the Mössbauer spectra for different polyvalent iodine compounds.

VII. IODONIUM ION AND IODONIUM YLIDE FORMATION REACTIONS

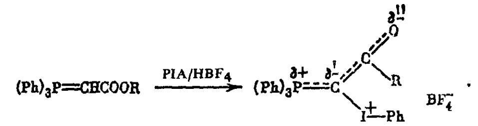
So many different methods of synthesis of iodonium salts and iodonium ylides have now been developed that they cannot be represented simply by any one scheme. However, most of them can be described by the equation given below:



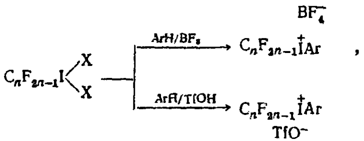
M=Li, Na; E = C, N.

In principle, any polyvalent iodine compounds can be used in iodonium ion formation reactions, but aryl iodosoacetates or iodoso-compounds are most frequently employed.[17] They can be generated *in situ* by oxidising aryl iodides.[263,264]

When the phosphonium ylide is treated with PIA in the presence of HBF_4, a double iodonium salt is obtained[265] (see also Moriarty et al.[266]):

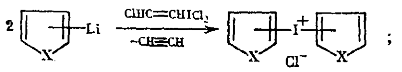


Derivatives of perfluoroiodosoalkanes were found to be extremely useful reagents for the synthesis of iodonium salts:[267–272]



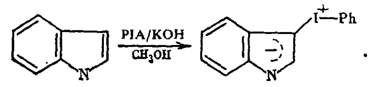
X=F, CF_3CO_2; Tf=CF_3SO_2 .

A unique iodonium ion forming agent is PIHT,[163,273–276] which can condense with trimethylsilyl derivatives of furan under neutral conditions to form furylphenyliodonium salts.[274] *trans*-Chlorovinyl iodosochloride is a convenient reagent for the synthesis of heterocyclic iodonium salts:[277–279]



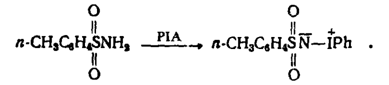
X=S, O, Cl

The reaction of PIA with indole (XC) leads to the formation of an ylide (XCI) with a carbon–iodine bond:[280]



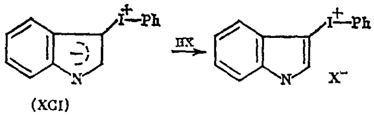
(XC) (XCI)

The interaction of PIA with toluene-p-sulphonamide affords an ylide with a nitrogen–iodine bond:[281]



$$n\text{-}CH_3C_6H_4\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}NH_2 \xrightarrow{PIA} n\text{-}CH_3C_6H_4\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\bar{N}-\overset{+}{I}Ph .$$

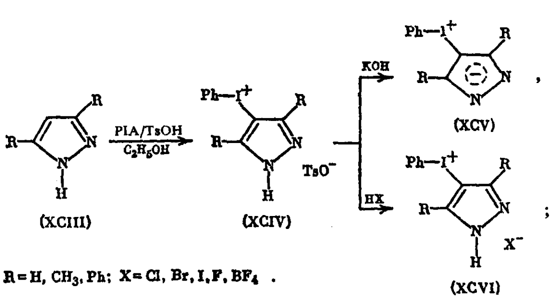
Iodonium salts are most closely related to iodonium ylides and they can sometimes be interconverted. The iodonium ylide (XCI) can be converted into the iodonium salts (XCII):[280]



(XCI)

X = TsO, BF_4, ClO_4 .

The iodonium salts (XCIV), obtained from pyrazoles (XCIII), give rise to the iodonium ylides (XCV) or the new iodonium salts (XCVI):[282]



(XCIII) (XCIV) (XCV) (XCVI)

R=H, CH_3, Ph; X=Cl, Br, I, F, BF_4 .

#According to these data,[262] the chlorine atoms in the molecule of phenyl iodosochloride are entirely equivalent, which fails to provide any kind of justification for the use of the term "aryliodonium chlorides" for aryl iodosochlorides, which can be encountered in some communications.

VIII. POLYMERS WITH TERVALENT IODINE

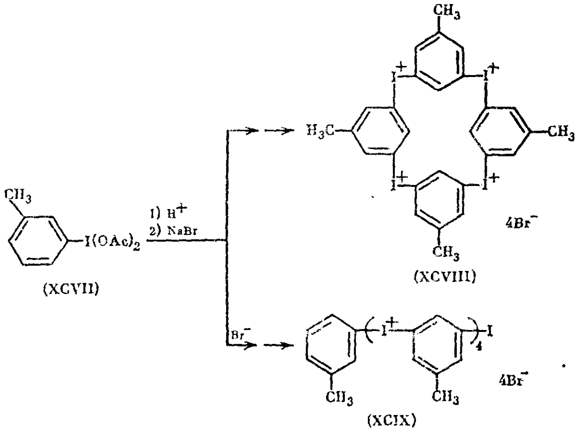
All these polymers can be arbitrarily divided into two groups. The first includes those in the molecules of which the tervalent iodine atom is used to link individual monomer units, while the second group comprises polymers whose monomer units are linked via other atoms and the polyvalent iodine atom enters into the composition of the macromolecule as a functional group.

Condensation of iodosobenzene with succinic anhydride, of PIA with adipic acid, and of phenyl iodosochloride with the silver salt of sebacic acid made it possible to obtain polymers in which the monomer units are linked by a tervalent iodine atom. They are solid brittle substances, insoluble in all the usual organic solvents under the normal conditions, but soluble on heating in some solvents, the dissolution being accompanied by degradation.[283] Unfortunately no data could be obtained about the structure of such polymers.

Polymers in which the monomer units are joined together with $-\overset{+}{I}-$groups have been synthesised:[284]

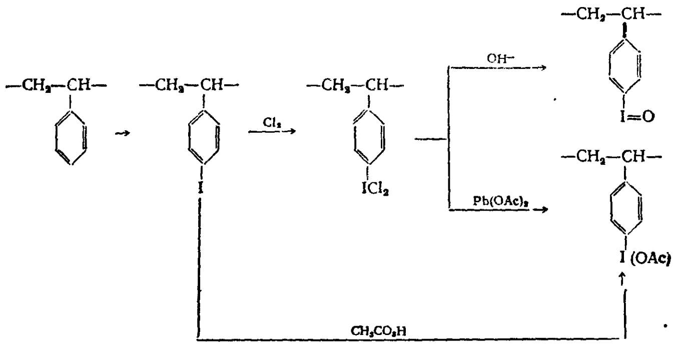
$$n\,\mathrm{Ph(CH_2)_3Ph}\xrightarrow[2)\ \mathrm{NaBr/H_2O}]{1)\ n(\mathrm{AcO})_2\mathrm{IC_6H_4I(OAc)_2}}-\left[-\overset{\mathrm{Br^-}}{\overset{+}{I}}-\mathrm{C_6H_4}-\overset{\mathrm{Br^-}}{\overset{+}{I}}-\mathrm{C_6H_4(CH_2)_3-C_6H_4}-\right]_n- .$$

m-Tolyl iodosoacetate (XCVII) forms cyclic or linear tetrameric iodonium ions (XCVIII) and (XCIX) in sulphuric acid:[284]

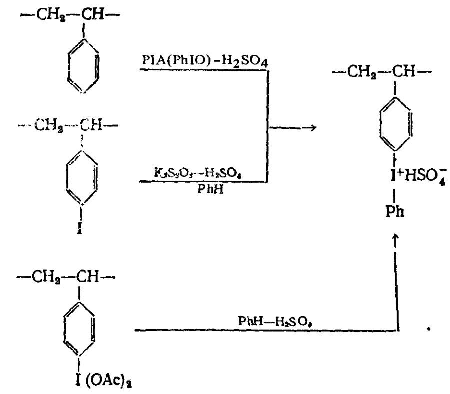


(XCVII) (XCVIII) (XCIX)

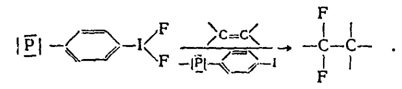
A series of polymers with polyvalent iodine, prepared on the basis of both linear and cross-linked polymers, are known.[285–296] The linear polystyrene can be iodinated in the presence of the oxidants P_2O_5–H_2SO_4 and HIO_3–H_2SO_4 on heating in nitrobenzene[288,289] in the presence of PITFA at room temperature in chloroform.[291] Poly(*p*-iodostyrene) can be converted into a polymer with polyvalent iodine by the same procedures as iodobenzene:



Polymeric iodonium salts based on linear polystyrene can be obtained with the aid of the reactions given below:[289]

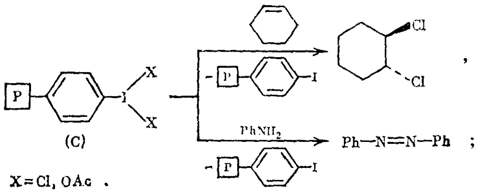


The cross-linked iodinated divyinylbenzene–styrene copolymer produces, on treatment with xenon difluoride, a polymeric reagent with iodosofluoride groups, which fluorinates olefins at room temperature with rearrangement:[292]



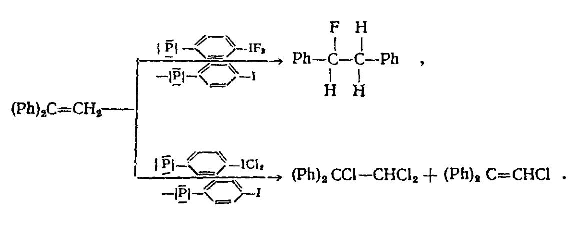
The spent polymer can be separated from the reaction product by simple filtration and can be reused after regeneration.[292]

The iodosochloride (C), obtained from the iodinated cross-linked divinylbenzene–styrene copolymer, reacts with cyclohexene to form *trans*-1,2-dichlorocyclohexane. The polymeric iodosoacetate (C) oxidises aniline to *trans*-azobenzene:[293]



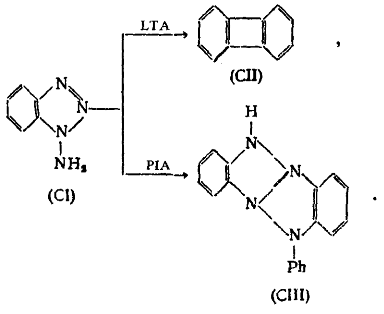
(C)

The reaction of 1,1-diphenylethylene with polymeric reagents based on cross-linked iodopolystyrene leads to various halogeno-derivatives:[294]

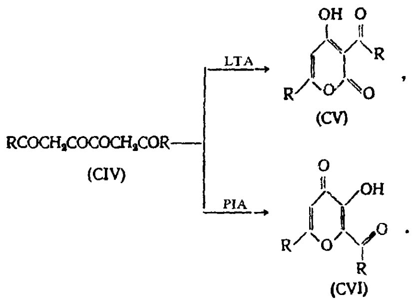


IX. CONCLUSION

Many chemists are under the impression that aryl iodosocarboxylates as oxidants are entirely similar to the popular reagent lead tetraacetate (LTA) (see, for example, Varvoglis[8]). However, in the 1980's a series of oxidation reactions were discovered, which proceed in a fundamentally different way, depending on whether the oxidant is LTA or PIA. For example, the oxidation of 1-aminobenzotriazole (CI) with LTA leads to the biphenylene (CII) in a high yield,[297] while in the oxidation of compound (CI) by PIA biphenylene is not formed at all and the main product is compound (CIII):[298]



By oxidising the tetraketone (CIV) with LTA or PIA, it is possible to obtain two isomeric pyrones (CV) and (CVI):[299]

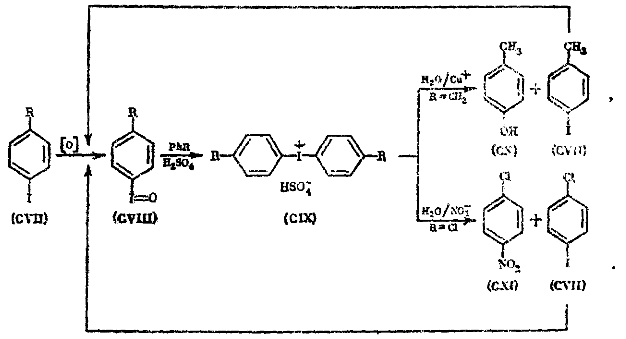


Bearing in mind the definite similarity between LTA and PIA in oxidation reactions, one should note one fundamental difference between these reagents. Their reduction products are lead diacetate in the former case and iodobenzene in the latter and to this day it is definitely easier to separate organic oxidation products from lead diacetate than from iodobenzene. It is noteworthy that PIA, in particular, and phenyl iodosocarboxylates in general can enter into the composition of polymers which are both soluble (for example, iodinated polystyrene) and insoluble (for example, the iodinated divinylbenzene–styrene copolymer). At the present time lead-containing polymers are not used in organic synthesis. These facts suggest that in the future the chemistry of polymeric iodosocarboxylate oxidants will develop. The products of the reduction of such reagents will be polymeric iodoarenes and they can be separated without special difficulty from reaction mixtures by simple filtration.

It is noteworthy that, as a chlorinating agent effecting the addition of chlorine to alkenes via an ionic mechanism, the polymeric iodosochloride resembles molecular chlorine rather than phenyl iodosochloride.[294]

Most attention should be devoted to multipurpose reagents for organic synthesis such as PITFA and PIHT.

There has been a remarkable study which demonstrated the possibility of obtaining p-cresol (CX) and p-chloronitrobenzene (CXI) by the iodonium ion formation reaction using iodo-derivatives of toluene or chlorobenzene (CVII), which proceeds via the corresponding iodo-derivatives (CVIII) and iodonium salts (CIX):[300]



Taking into account all the foregoing factors, one may conclude that, together with iodonium salts, the most important representative of organic compounds of tervalent iodine are aryl iodosocarboxylates and that new major discoveries are to be expected in the first place in these two fields.

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The σ Constants of Substituents Containing Silicon Subgroup Elements

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The general aspects of the correlation equations linking the structure and reactivity of compounds of silicon subgroup elements are examined. Taking into account the specific features of the intramolecular interactions in the organoelemental compounds, the σ constants of substituents containing silicon, germanium, and tin atoms have been analysed.
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I. INTRODUCTION

The search for and investigation of the relations between the chemical structure of molecules and their reactivity is one of the fundamental problems in chemistry. The most significant advances in physical organic chemistry, achieved in this field during the last few decades, are associated with the use of the so called correlation equations based on the principle of the linear relation between the free energy changes (LFE).[1-18] The essential feature of the LFE principle is as follows.[1,4] If the molecule consists of the reacting group A and the non-reacting substituent X, then (a) the change in the logarithm of the rate constant *k* induced by the influence of X is linearly related to the change in the logarithm of the equilibrium constant *K* for the same reaction [Eqn.(1)]:

$$\delta_X \lg k_1 = a_1 \delta_X \lg K\,, \qquad (1)$$

and (b) the changes in lg *k* and lg *K* induced by the influence of X, for a reaction I with participation of the group A_1 are linearly related to the corresponding changes for another reaction II with participation of the same group A_1 and also for reaction II with participation of another group A_2:

$$\delta_X \lg k_1 = b_{12} \delta_X \lg k_2 = a_2 b_{12} \delta_X \lg K_2\,, \qquad (2)$$

where k_1 and K_1 refer to reaction I and k_2 and K_2 refer to reaction II, a_1, a_2, and b_{12} are independent of X but do depend on the reactions considered, and δ_X is an operator reflecting the influence of the change in the substituent X on *k* and *K*.

Experimental data on the basis of which the LFE principle has been formulated have been analysed in a number of studies.[1,5,6,9,18,19] By comparing the ionisation constants of substituted benzoic acids K_a with the constant for the unsubstituted acid K_0 in water at 25 °C, it is possible to obtain from Eqn.(1) the constants σ characterising the substituents

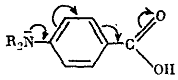
$$\sigma = \lg K_a - \lg K_0 \qquad (3)$$

and then the familiar Hammett equation:[1]

$$\lg k - \lg k_0 = \rho\sigma, \qquad (4)$$

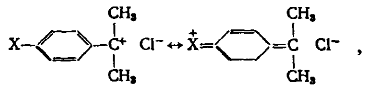
The reaction constant ρ in Eqn.(4) characterises the sensitivity of the reaction to the electronic effects of the substituents compared with the constant 1.00 adopted for the dissociation of benzoic acids.

Thus the first method of determining the Hammett σ_m and σ_p constants for *meta*- and *para*-substituents (including organoelemental substituents) in the benzene ring involves the study of the ionisation constants of benzoic acids or the rate constants *k* for the reaction involving the side chain of benzene derivatives. However, this procedure cannot be used to calculate the σ constants for *ortho*-substituents, since their influence on the reaction centre is determined not only by electronic effects but also by steric effects. An important characteristic feature of the Hammett σ_p constants (in contrast to the σ_m constants) for π-electron-donating substituents (the *+M* types of substituents NR_2, OR, and $CH_2.EP_3$, where *E* is a silicon subgroup element) is their dependence on the direct polar conjugation between these substituents and their reaction centres, which can be described, for example, by the following schemes:



Therefore, in order to estimate the degree of interaction between the substituent and the ring, it is essential to disrupt in such cases the direct polar conjugation system. For example, one can use data for the ionisation constants of the acids $XC_6H_4CH_2COOH$. Similar procedures have been used in a number of investigations.[20-24]

As a result, the constants σ^0 have been obtained for *+M* type *para*-substituents.[11,13] The σ_p^+ constants have been introduced[15,25] to characterise *para*-substituents of the *+M* type which are involved in direct polar conjugation with the electron-deficient reaction centre. Thus the stabilisation of the transition state in the reaction involving the solvolysis of cumenyl chlorides by substituents X of this kind (for example, the group CH_3O), i.e.



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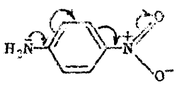
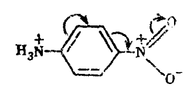
is associated mainly with the enhancement of the electron-donating properties of the group X, i.e. with the increase of the absolute values of the constants σ_p^+ for these substituents compared with the Hammett σ_p constants. The constants σ_m^+ and σ_m for the *meta*-substituents are virtually identical.

In order to characterise the electron-accepting substituents of the *−M* type (NO_2, CN, CHO, etc.), which are involved in direct polar conjugation with the reaction centre, σ_p^- constants have been introduced.[1,18,19] The enhancement of the electron-accepting properties of the NO_2 group as a substituent ($\sigma_p^- > \sigma_p$), manifested in the ionisation of aniline derivatives, can be accounted for by direct polar conjugation:



which leads to a decrease of the basicity of *p*-nitroaniline. There is no direct polar conjugation in the *p*-nitroanilinium ion:[10]



The constants σ_m^- and σ_m for *meta*-substituents are virtually identical. The σ constants discussed above are represented by the sum of the inductive (σ_I) and resonance (σ_R) contributions: $\sigma = \sigma_I + \sigma_R$. In order to estimate the inductive effect and hence resolve σ into its components, methods based on the LFE principle and the hypothesis that the free energy of activation can be represented by the sum of independent contributions due to the inductive, resonance, and steric effects have been developed.[2] For quantitative estimates of the inductive effects, the following factors were studied: the ionisation of bicyclo[2.2.2]octane-1-carboxylic acids;[11,26,27] the hydrolysis of the aliphatic acid esters XCH_2COOR;[2,3] the ionisation of substituted aliphatic acids;[28] the reactivity of aromatic compounds;[29,30] the chemical shifts of the signals of the ^{19}F nuclei in the NMR spectra of *meta*-substituted fluorobenzenes.[16,31] The constants σ_I, or quantities proportional to them, were obtained in the above studies for a large number of substituents, including those containing silicon subgroup elements.

The problem of the quantitative estimation of the inductive effect has been discussed in greater detail in a number of studies,[9-12,19] in which the possibility of resolving the σ constants into the inductive (σ_I) and resonance (σ_R) components was also analysed:

$$\sigma_R = \sigma_p - \sigma_I\,, \tag{5}$$

$$\sigma_R^0 = \sigma_p^0 - \sigma_I\,, \tag{6}$$

$$\sigma_R^+ = \sigma_p^+ - \sigma_I\,, \tag{7}$$

$$\sigma_R^- = \sigma_p^- - \sigma_I\,. \tag{8}$$

It has been emphasised[11] that the resonance constants of type σ_R, determined from Eqns.(5)–(8), are least accurate, since they depend on the errors in the determination of the constants σ_p and σ_I. The constants σ_R^0 are calculated from NMR and IR spectroscopic data.[16,31-33] A series of physicochemical and physical methods for the determination of the σ constants of substituents have been described in the review literature[11-13] and certain methods will be considered below.

We may note that, despite the wide variety of methods for the determination of σ constants and the use of different scales for the latter, when account is taken of the electronic effects of substituents, only the constants defined by Eqns.(5)–(8) are usually employed. This group of relations does not include the constants for complex aromatic systems and *ortho*-substituents and also constants characterising the steric effects of substituents. It is clear from the foregoing that the correlation equations relating the chemical structure and reactivity of compounds, based on the LFE principle, are empirical. For this reason, since the publication of the first[1] and subsequent studies[34,35] (see also the relevant reviews[8,12,19,36,37]), attempts have been frequently made to secure a justification of the system of Hammett–Taft constants. As early as the 1950's, it was established[34,35] with the aid of approximate quantum-chemical methods that the σ constants of substituents in the benzene ring are proportional to the change, induced by these substituents, in electron density on the carbon atoms in the *meta*- and *para*-positions in the ring and hence also on the reaction centre linked to these carbon atoms. On the one hand, these studies fundamentally clarified the physical significance of the σ constants, and, on the other hand, they served as the basis for an enormous number of investigations devoted to the analysis of the relations between the σ constants and various physical properties of organic and organoelemental compounds.

The results of some of these studies, which can be treated as sources of useful information about the σ constants of substituents incorporating the silicon subgroup elements and also about the specific features of the intermolecular interactions in organoelemental compounds of Group IVB elements, will be considered below in greater detail. In recent years, additional data, confirming the interpretation of the physical significance of the σ constants formulated in the 1950's, have been obtained with the aid of modern non-empirical quantum-chemical methods. It has been established for benzene derivatives[37,38] and ethylene and acetylene derivatives[39,40] that the π-electronic charge on the substituent is linearly related to the corresponding σ_R^0 constants.

However, the theoretical justification of both the correlation equations and of the LFE principle itself is inadequate. Furthermore, there exist a number of experimental limitations. For this reason, the σ constants can be used only with a certain degree of caution. The present review does not discuss the contradictions between the LFE principle and Hammond's postulate[6,9,10] and the influence of the field effects and bond polarisation on the σ_I constants is not dealt with in detail.[41,42] We may note that, in choosing the most reliable values of the σ constants (see below), account was taken of the dependence of the constant σ on temperature,[43] the solvent, the type of conducting system, and the nature of the reaction centre. Furthermore the hyperconjugation effects,[44] which are more important for organoelemental compounds than for organic compounds, and also the specific features of the steric effects in compounds of silicon subgroup elements[45] were taken into account.

It is essential to note that the limited amount of the available literature data and also in many instances the inadequate reliability (see below) of some of the σ constants preclude so far the formulation of reliable (statistical) values[11] for these quantities referring to substituents containing silicon subgroup elements. Therefore, our choice of the most and least reliable σ constants was made taking into account the views of the authors of the original publications and our own. As literature data accumulate and methods for the determination of σ constants develop and improve, a correction of many of their values will become inevitable.

II. METHODS FOR THE DETERMINATION OF THE σ CONSTANTS OF ORGANOELEMENTAL GROUP IVB SUBSTITUENTS

The methods for the determination of the σ constants of organoelemental substituents can be divided into two groups. The first group includes the physical (mainly spectroscopic) methods for the determination of σ constants. Different versions of NMR,[16,31,44-59] the IR spectroscopy of individual compounds and molecular complexes,[32,33,60–64] the UV spectroscopy of charge-transfer complexes (CTC),[38,65–67] the ionisation potentials[66] and dipole moments[68] of compounds with organoelemental substituents, as well as many other less common physical methods have been employed. The second group includes methods for the determination of the σ constants of organoelemental compounds based on the study of the chemical properties of various compounds containing such substituents.

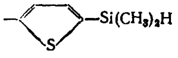
Overall, the use of physical methods is preferable. The errors of the determination associated with the possibility of the involvement in the reaction of not only the main reaction centre but also of the organoelemental substituents ER_3 (E is a silicon subgroup element), whose E atom may be solvated in consequence of the high reactivity of organoelemental compounds and E–C bonds may be cleaved, are reduced to a minimum in this instance. The values of σ found without a sufficiently correct estimation of such complicating factors cannot therefore be regarded as fully reliable.

The Tables presented below indicate, together with the values of the σ constants, also the methods of their determination and (in the footnotes to the Tables) a brief description of the characteristics of the methods. In the Tables, the most reliable σ constants are included in square brackets and the least reliable ones are in round brackets. If experimental literature data were used to calculate the σ constants, the number of the corresponding literature reference in the Table is followed by an asterisk.

III. ANALYSIS OF THE σ CONSTANTS

The σ constants are a source of quantitative information about the electronic effects of substituents containing the elements E. The tasks dealt with in this Section are a systematic arrangement and analysis of such information and also the selection (in accordance with the principles indicated above) of the most and least reliable values of σ.

Table 1. The constants σ_I of silicon-containing substituents.

Substituent	σ_I	Method of determination	Refs.
SiH_3	−0.05	NMR-C-B	[53]
SiH_3	−0.04	NMR-C-B	[80]
SiH_3	+0.01	NMR-F-B	[81]
$SiH(CH_3)_2$	−0.02	NMR-F-B	[81]
$Si(CH_3)_3$	−0.24	NMR-C-B	[53]
$Si(CH_3)_3$	[−0.15]	IR-SiH	[64]
$Si(CH_3)_3$	−0.15	NMR-C-B	[80]
$Si(CH_3)_3$	−0.15	X-1	[82]
$Si(CH_3)_3$	−0.13	X-2	[28]
$Si(CH_3)_3$	−0.12	X	[2]
$Si(CH_3)_3$	−0.11	IR-M-H	[62]
$Si(CH_3)_3$	−0.10	X	[8]
$Si(CH_3)_3$	−0.10	NMR-C-B	[17]
$Si(CH_3)_3$	−0.09	NMR-C-S, NMR-H-S	[57]
$Si(CH_3)_3$	−0.04	NMR-F-B	[81]
$Si(CH_3)_3$	(−0.03)	NMR-F-B	[46]
$Si(CH_3)_3$	+0.02	NMR-F-N	[46]
$Si(C_2H_5)_3$	−0.18	IR-SiH	[64]
$Si(C_2H_5)_3$	−0.18	IR-M-H	[62]
$Si(C_2H_5)_3$	−0.24	NMR-C-B	[53]
$Si(n\text{-}C_3H_7)_3$	−0.27	NMR-C-B	[53]
$Si(iso\text{-}C_4H_9)_3$	−0.36	NMR-C-B	[53]
$Si(CH_3)_2CH{=}CH_2$	−0.03	NMR-F-B	[81*]
$Si(CH{=}CH_2)_3$	−0.19	NMR-C-B	[53]
$Si(CH_3)_2C_3H_5$	+0 02	NMR-F-B	[81]
$Si(CH_3)(C_6H_5)_2$	+0.07	NMR-F-B	[81]
$Si(C_6H_5)_3$	(−0.17)	NMR-C-B	[53]
$Si(C_6H_5)_3$	−0.15	NMR-C-B	[80]
$Si(C_6H_5)_3$	−0.19	IR-M-H	[62]
$Si(C_6H_5)_3$	(+0.13)	NMR-F-B	[81]
$Si(C{\equiv}CH)_3$	+0.08	NMR-C-B	[53]
$Si[N(CH_3)_2]_3$	(−0.20)	NMR-C-B	[53]
$Si[N(CH_3)_2]_3$	−0.11	NMR-C-B	[80(
$Si[N(CH_3)_2]_3$	−0.04	NMR-F-B	[81]
$Si(CH_3)(C_6H_5)OCH_3$	−0.22	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OC_2H_5$	−0.25	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OC_3H_7$	−0.25	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH(CH_3)_2$	−0.31	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OC_4H_9\text{-}n$	−0.25	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OC_4H_9\text{-}iso$	−0.25	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OC_4H_9\text{-}s$	−0.31	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH_2C_6H_5$	−0.24	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH_2CH_2Cl$	−0.30	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH_2C{\equiv}CH$	−0.30	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH_2CH_2CH_2CN$	−0.18	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)OCH_2CF_3$	−0.06	NMR-C-B	[83]
$Si(OH)_3$	−0.22	NMR-C-B	[53]
$Si(OCH_3)_3$	(−0.07)	NMR-C-B	[53]
$Si(OCH_3)_3$	0.00	NMR-F-B	[81]
$Si(OCH_3)_3$	+0.01	NMR-C-B	[80]
$Si(OCH_3)_3$	+0.01	NMR-C-B	[52]
$Si(OC_2H_5)_3$	(−0.18)	NMR-C-B	[52]
$Si(OC_2H_5)_3$	−0.13	NMR-C-B	[53]
$Si(OC_2H_5)_3$	−0.08	NMR-C-B	[80]
$Si(OC_2H_5)_3$	−0.04	NMR-F-B	[81]
$Si(OC_3H_7\text{-}n)_3$	−0.19	NMR-C-B	[80]
$Si(OC_3H_7\text{-}iso)_3$	−0.24	NMR-C-B	[53]
$Si(OC_3H_7\text{-}iso)_3$	−0.16	NMR-C-B	[52]
$Si[OC(CH_3)_3]_3$	(−0.43)	NMR-C-B	[53]
$Si(OC_6H_5)_3$	(−0.14)	NMR-C-B	[80]
$Si(OC_6H_5)_3$	−0.05	NMR-C-B	[53]
$Si(CH_3)_2OSi(CH_3)_3$	−0.13	X-2	[28]
$Si[OSi(CH_3)_3]_3$	−0.29	NMR-C-B	[53]
$\overline{\overset{\downarrow}{Si}(OCH_2CH_2)_3N}$	(−0.56)	NMR-C-B	[53]
$\overline{\overset{\downarrow}{Si}(OCH_2CH_2)_3N}$	−0.40	NMR-C-B	[80]
$\overline{\overset{\downarrow}{Si}(OCH_2CH_2)_3N}$	−0.40	NMR-C-B	[52]
$\overline{\overset{\downarrow}{Si}(OCH_2CH_2)_3N}$	−0.2	Ph	[84]
$\overline{\overset{\downarrow}{Si}(OCH_2CH_2)_3N}$	−0.2	Ph	[85]
$\overline{\overset{\downarrow}{Si}(OCH_2CH_2)_3N}$	−0.15÷−0,2	Ph	[86]
$Si(OCH_2CH_2NH_2)_3$	−0.10	NMR-C-B	[53]
$Si(OCOCH_3)_3$	+0.07	NMR-C-B	[53]
$Si(OCOCF_3)_3$	+0.76	NMR-C-B	[53]
$Si(SC_2H_5)_3$	+0.06	NMR-C-B	[53(
$Si(CH_3)_2F$	+0.08	NMR-F-B	[81]
SiF_3	+0.42	NMR-F-B	[81]
SiF_3	+0,43	NMR-C-B	[80]
SiF_3	+0.43	NMR-C-B	[53]
SiF_3	(+0.57)	NMR-M-H	[62]
$Si(CH_3)_2Cl$	(+0.05)	IR-M-H	[62]
$Si(CH_3)_2Cl$	+0.11	NMR-F-B	[81]
$Si(CH_3)Cl_2$	+0.21	IR-M-H	[62]
$Si(CH_3)Cl_2$	+0.24	NMR-F-B	[81]
$SiCl_3$	(+0.15)	NMR-C-B	[80]
$SiCl_3$	+0.21	NMR-C-B	[53]
$SiCl_3$	+0.36	IR-M-H	[62]
$SiCl_3$	[+0.39]	NMR-F-B	[81*]
$Si(CH_3)ClBr$	+0.25	NMR-F-B	[81*]
$SiBr_3$	(−0.09)	NMR-C-B	[80]
$SiBr_3$	+0.08	NMR-C-B	[53]
$SiBr_3$	+0.29	IR-M-H	[62]
$SiBr_3$	[+0.39]	NMR-F-B	[81]
$Si(CH_3)_2CH_2CH_2CF_3$	+0.08	NMR-F-B	[81*]
$Si(CH_3)_2CH_2Cl$	+0.06	NMR-F-B	[81*]
$CH_2Si(CH_3)_3$	−0.10	NMR-C-S, NMR-H-S	[57]
$CH_2Si(CH_3)_3$	−0.08	NMR-F-B	[87]
$CH_2Si(CH_3)_3$	−0.07	NMR-F-B	[16]
$CH_2Si(CH_3)_3$	−0.06	NMR-F-B	[88]
$CH_3Si(CH_3)_3$	[−0.05]	IR-SiH, Ph	[89]
$CH_2Si(CH_3)_3$	−0.05	X-2	[28]
$CH_2Si(CH_3)_3$	−0.04	X	[2]
$CH_2Si(CH_3)_3$	(+0.01)	NMR-F-N	[88]
$CH_2Si(C_6H_5)_3$	+0.01	NMR-F-N	[88]
$CH_3Si(OCH_3)_3$	−0.10	NMR-F-B	[90]
$CH_2\overline{\overset{\downarrow}{Si}(OCH_2CH_2)_3N}$	−0.36	NMR-F-B	[90]
$CH_2CH_2Si(CH_3)_3$	−0.04	X-2	[28]
$CH_2CH_2Si(CH_3)_3$	−0.03	IR-SiH, Ph	[89]
$CB_{10}H_{10}CSi(CH_3)_2H$	+0.30÷+0.35	Ph	[91]
$C_6H_4Si(CH_3)_2H$	+0.07÷+0.12	Ph	[91]
	+0.10÷+0.15	Ph	[91]
$COOCH_2Si(OC_2H_5)_3$	+0.10	NMR-C-B	[92]
$COOCH_2\overline{\overset{\downarrow}{Si}(OCH_2CH_2)_3N}$	−0.05	NMR-C-B	[92]
$COOCH_2SiF_3$	+0.61	NMR-C-B	[92]
$NHSi(CH_3)_3$	+0.09	NMR-C-B	[93]
$OSi(CH_3)_3$	+0.05	NMR-C-B	[93]
$-O[Si(CH_3)_2O]_3-$	∼+0.3	Ph	[93]

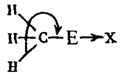
Please note notation over page.

Table 1 (continued).

Notation: NMR-C-B—analysis of the chemical shifts of the signals of the *meta*- and *para*-carbon atoms in the ^{13}C-derivatives of benzene. The specific form of the relations between the chemical shifts or their differences and the constants σ, σ_R^0, and ρ^* has been indicated in a series of communications;[44–55] NMR-F-B—analysis of the chemical shifts δ in the ^{19}F NMR spectra of the *meta*-substituted (δ_m) and *para*-substituted (δ_p) fluorobenzenes. The most widely used is the method of Taft and co-workers[16,31] using the relations $\delta_m = -7.1\ \sigma_I + 0.60$ and $\delta_p = 7.1\ \sigma_I - 29.5\ \sigma_R^0 + 0.60$. The chemical shifts are measured relative to the shift of fluorobenzene for solutions in chloroform; IR-SiH—analysis of the stretching vibration frequency of the Si–H bond in the IR spectra of silane derivatives;[64] X-1–the study of the p*K* of substituted benzoic acids;[69,70] X-2–the study of the p*K* of substituted acetic acids;[28] X—on the basis of reactivity data but using less common methods; IR-M-H—analysis of the vibrational spectra and force constants of the M–H bonds (M = silicon subgroup element);[62] NMR-C-S—analysis of the chemical shifts of the signals of the carbon atoms in the vinyl group and the benzene ring in the ^{13}C NMR spectra of 4-substituted styrenes $XC_6H_4.CH{=}CH_2$;[56,57] NMR-H-S—analysis of the chemical shifts in the ^1H NMR spectra of 4-substituted styrenes $XC_6H_4.CH{=}CH_2$;[56,57] NMR-F-N—analysis of the chemical shifts in the ^{19}F NMR spectra of β-fluoronaphthalenes;[46] Ph—on the basis of physical research methods but using less common procedures.

1. The Inductive Constants σ_I

The constants σ_I characterise quantitatively the inductive effects of the substituents EX_3, where X are various groups. The changes in the values of σ_I for EX_3 and CX_3 with fixed X and variable E reflect the changes in the electronegativities of the Group IV elements E. However, the electronegativities of the Group IV elements E have not been generally accepted. Thus, according to Marrot and Maire,[75] the electronegativities of the elements E and groups of the type $E(C_2H_5)_nCl_{3-n}$ diminish in the sequence C > Ge > Si > Sn. However, according to other data,[76] the character in the changes in the electronegativities is different: C(2.55) > Pb(2.33) > Ge(2.01) > Sn(1.96) > Si(1.90) (the numerical values are given in brackets). The differences between these two series are caused not only by the different accuracies of the methods for the determination of electronegativity but also by more profound causes.[44,77] One of these is the effect (together with the inductive effect) of the σ,σ conjugation, whose influence increases in the sequence C < Si < Ge < Sn < Pb and depends on the type of substituents linked to E. For this reason, both inductive and hyperconjugation contributions are significant for the constants of certain substituents EX_3.[78] We may note that, in systems of the type



the contribution of σ,σ conjugation increases with the increase of the atomic number of E and with enhancement of the electron-accepting properties of X.[44]

The second cause is the conjugation within the substituent EX_3, which influences its electronegativity. If X is an atom or fragment with unshared electron pairs or an αβ-unsaturated hydrocarbon group, then, as will be shown in greater detail in the analysis of the constants σ_R, resonance effects arise. The role of the latter increases with increase of the σ_R for the groups X and also in the sequence Sn < Ge < Si and with increase of the effective positive charge on E, which depends on the fourth substituent linked to E.[79]

Table 2. The constants σ_I of germanium-, tin-, and lead-containing substituents.

Substituent	σ_I	Method of determination	Refs.
$Ge(CH_3)_3$	−0.12	IR-M-H	[62]
$Ge(CH_3)_3$	[−0.11]	IR-SiH, Ph	[89]
$Ge(CH_3)_3$	−0.10	NMR-C-S, NMR-H-S	[57]
$Ge(CH_3)_3$	−0.01	X	[46]
$Ge(CH_3)_3$	+0.06	NMR-F-N	[46]
$Ge(C_2H_5)_3$	−0.19	IR-M-H	[62]
$Ge(C_2H_5)_3$	−0.13	IR-SiH	[64]
$Ge(OCH_3)_3$	+0.37	NMR-C-B	[51]
$Ge(OC_2H_5)_3$	+0 29	NMR-C-B	[51]
$Ge(OC_3H_7\text{-iso})_3$	+0.19	NMR-C-B	[51]
$Ge(OC_4H_9\text{-t})_3$	−0.01	NMR-C-B	[51]
$\overline{Ge(OCH_2CH_2)_3N}$	−0.23	NMR-C-B	[51]
GeF_3	+0.74	NMR-F-B	[94]
$GeCl_3$	+0.63	NMR-F-B	[94]
$GeBr_3$	+0.59	NMR-F-B	[94]
$CH_2Ge(CH_3)_3$	−0.10	NMR-C-S, NMR-H-S	[57]
$CH_2Ge(CH_3)_3$	[−0.04]	IR-SiH, Ph	[89]
$CH_2Ge(CH_3)_3$	−0.04	NMR-F-B	[88]
$CH_2Ge(CH_3)_3$	(+0.02)	NMR-F-B	[88]
$CH_2Ge(C_2H_5)_3$	−0.05	IR-SiH, Ph	[89]
$CH_2Ge(C_6H_5)_3$	+0.02	NMR-F-N	[88]
$Sn(CH_3)_3$	−0.15	IR-M-H	[62]
$Sn(CH_3)_3$	[−0.13]	IR-SiH, Ph	[89]
$Sn(CH_3)_3$	−0.11	NMR-C-S, NMR-H-S	[57]
$Sn(CH_3)_3$	0 0	X	[46]
$Sn(CH_3)_3$	+0.01	NMR-F-B	[95]
$Sn(CH_3)_3$	(+0.09)	NMR-F-N	[46]
$Sn(C_2H_5)_3$	+0.02	NMR-F-B	[95]
$Sn(\text{н-}C_4H_9)_3$	+0.02	NMR-F-B	[95]
$Sn(C_6H_5)_3$	+0.18	NMR-F-B	[96, 97]
$Sn(C_6H_5)_3$	+0.15 ($CDCl_3$)	NMR-F-B	[95]
$Sn(C_6H_5)_3$	+0.20 (CCl_4, $(CD_3)_2CO$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}4)_3$	+0,25 ($(CD_3)_2CO$, $CDCl_3$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}4)_3$	+0.28 (CCl_4)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	+0.28 ($CDCl_3$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	+0.26 ($(CD_3)_2CO$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	+0.33 (CCl_4)	NMR-F-B	[95]
$SnCl_3$	+0.82 ($CDCl_3$)	NMR-F-B	[95]
$SnCl_3$	+0.42 ($(CD_3)_2CO$)	NMR-F-B	[95]
$SnCl_3$	+0.80 (CCl_4)	NMR-F-B	[95]
$CH_2Sn(CH_3)_3$	−0.11	NMR-C-S, NMR-H-S	[57]
$CH_2Sn(CH_3)_3$	[−0.05]	IR-SiH, Ph	[89]
$CH_3Sn(CH_3)_3$	−0.04	NMR-F-B	[88]
$CH_3Sn(CH_3)_3$	(+0.05)	NMR-F-N	[88]
$CH_2Sn(C_6H_5)_3$	0.0	NMR-F-B	[96, 97]
$CH_2Sn(C_6H_5)_3$	+0.07	NMR-F-N	[88]
$CH_2CH_2Sn(CH_3)_3$	−0.02	IR-SiH, Ph	[89]
$OSn(C_2H_5)_3$	+0.08	NMR- F-B	[98, 99]
$OSn(C_6H_5)_3$	+0.10	NMR-F-B	[99]
$SSn(C_2H_5)_3$	+0.23	NMR-F-B	[100]
$SSn(C_6H_5)_3$	+0.11	NMR-F-B	[97, 99]
$Pb(CH_3)_3$	−0.12	NMR-C-S, NMR-H-S	[57]
$Pb(CH_3)_3$	+0.03	X	[46]
$Pb(CH_3)_3$	+0.12	NMR-F-N	[46]
$Pb(C_6H_5)_3$	+0.22	NMR-F-B	[96, 97]
$CH_2Pb(CH_3)_3$	−0.12	NMR-C-S, NMR-H-S	[57]
$CH_2Pb(CH_3)_3$	[−0.04]	NMR-F-B	[88]
$CH_2Pb(CH_3)_3$	+0.06	NMR-F-N	[88]
$CH_2Pb(C_6H_5)_3$	0.0	NMR-F-B	[96, 97]
$CH_3Pb(C_6H_5)_3$	+0.07	NMR-F-N	[88]
$OPb(C_6H_5)_3$	+0.06	NMR-F-B	[99]
$SPb(C_6H_5)_3$	0,00	NMR-F-B	[99]

Notation: The solvents are indicated in brackets; for the significance of the designation of the methods, see the footnote to Table 1.

Ultimately the effective charge on the atom E changes in a complex manner and the electronegativity of the group EX_3 depends not only on the atom E but also on the type of substituent X and the organoelemental molecule as a whole. For this reason, the constants σ_I for organoelemental substituents (Tables 1 and 2) can be regarded as constants only by convention. As experimental data accumulate, a subsystem of σ_I constants will apparently be created for each comparatively narrow type of compounds.

On the basis of the data in Tables 1 and 2, one may reach several conclusions of a general character. For a fixed atom E, the constants σ_I of substituents of the type EX_3 vary in parallel with the enhancement of the electron-accepting properties of the group X: Alk < C_6H_5 < OAlk < Br < Cl < F. A higher value of σ_I corresponds to the substituent CH_2EX_3 than to the substituent EX_3. This is associated primarily with the electronegativity of the carbon atom, which exceeds the electronegativity of other Group IVB elements, which also agrees with the higher values of σ_I for $CAlk_3$ compared with $EAlk_3$. For example, the values of σ_I for $E(CH_3)_3$ are −0.07 (E = C[11]), −0.15 (E = Si), −0.11 (E = Ge), and −0.13 (E = Sn). However, constants σ_I which in many cases appreciably exceed the analogous values for carbon compounds correspond to the substituents $EHal_3$; 0.41–0.45 (CF_3); 0.30–0.41 (CCl_3); 0.26 (CBr_3).[11] We may note that, among the constants σ_I for halogenoalkyl groups, appreciable anomalies are also observed which cannot be accounted for solely from the standpoint of electronegativity. It is believed[101] that these anomalies are caused by the field effect, which has also been confirmed by data[42] indicating the predominance of the field effect over electronegativity for substituents of this type.

Smaller σ_I constants correspond to the silantranyl and germantranyl groups than to the corresponding trialkoxy-derivatives, which may be associated with the decrease of the electronegativity of the central atom owing to the partial electron transfer to this atom from nitrogen. The constants σ_I for the substituents $OEAlk_3$ and $SSnAlk_3$ are lower than the corresponding values for the analogous carbon derivatives apparently mainly owing to the more pronounced electron-donating properties of the groups $EAlk_3$ (compared with alkyl groups) (the constants σ_I for OAlk and SAlk are 0.3–0.2).[11]

2. The Resonance Constants σ_R^0

The constants σ_R^0 characterise the ability of substituents to be conjugated with n-donor groups or π-systems. Being involved in conjugation, the substituents EX_3 are electron donors (negative σ_R^0) (Tables 3 and 4). In this respect, the substituents EX_3 differ sharply from their carbon analogues CX_3. On the other hand, weakly electron-donating properties, arising in consequence of hyperconjugation, are typical for the substituents CX_3. Electronegative groups X can exhibit weak electron accepting properties.

The traditional interpretation of the resonance electron-accepting properties of EX_3 is based on the idea that the unoccupied *nd* orbitals of the atoms E participate in conjugation with *n*- or π-donor fragments D in compounds of the type $D{-}EX_3$ [$(p-d)\pi$ interaction]. This problem has been discussed in greater detail by Egorochkin and Khorshev.[79] Clearly the resonance interactions between the fragments D and EX_3 are determined both by the electron-donating properties of D and the electron-accepting properties of EX_3. Therefore, by fixing the fragment EX_3 and varying the fragment D, it is possible to vary the degrees of resonance interactions between EX_3 and D. It follows from the general theory[111] and experimental studies on organosilicon and organogermanium compounds[77,79] that the character of the variation of the degree of the $(p-d)\pi$ interaction between the fixed fragment EX_3 and the variable fragment D is determined by the σ_R constants of D. On the other hand, if both fragments EX_3 and D, vary, then the effective positive charge on the atom E becomes decisive. The constants σ_R^0 can therefore be regarded as characteristics of substituents of type EX_3 only for a fixed fragment D; an analogous situation obtains also for the constants σ_I.

Table 3. The constants σ_R^0 of silicon-containing substituents.

Substituent	σ_R^0	Method of determination	Refs.
SiH_3	+0.08	NMR-C-B	[53, 80]
SiH_3	+0.09	NMR-F-B	[81]
$SiH(CH_3)_2$	+0.06	NMR-F-B	[81]
$Si(CH_3)_3$	+0.02	IR-B	[102]
$Si(CH_3)_3$	+0.03	NMR-C-S1	[50]
$Si(CH_3)_3$	+0.04	NMR-F-B	[46]
$Si(CH_3)_3$	+0.04	X	[103]
$Si(CH_3)_3$	+0.04	NMR-C-B	[17]
$Si(CH_3)_3$	+0.04	Ph	[104]
$Si(CH_3)_3$	+0.04	IR-HB-A	[63]
$Si(CH_3)_3$	+0.05	NMR-C-B	[50, 53]
$Si(CH_3)_3$	[+0.05]	NMR-F-B	[81]
$Si(CH_3)_3$	+0.06	Ph	[8]
$Si(CH_3)_3$	+0.07	NMR-C-S, NMR-H-S	[57]
$Si(CH_3)_3$	+0.09	IR-B	[105]
$Si(CH_3)_3$	+0.10	NMR-C-B	[80]
$Si(CH_3)_3$	+0.04	IR-HB-A	[63]
$Si(C_2H_5)_3$	+0.05	NMR-C-B	[50, 53]
$Si(n\text{-}C_3H_7)_3$	+0.05	NMR-C-B	[53]
$Si(iso\text{-}C_4H_9)_3$	+0.05	NMR-C-B	[53]
$Si(t\text{-}C_4H_9)_3$	+0.05	NMR-C-B	[50]
$Si(CH_3)_2CH{=}CH_2$	+0.05	NMR-F-B	[81]
$Si(CH{=}CH_2)_3$	+0.08	NMR-C-B	[53]
$Si(C{\equiv}CH)_3$	+0.14	NMR-C-B	[50, 53]
$Si(CH_3)_2C_6H_5$	+0.05	NMR-F-B	[81]
$Si(CH_3)(C_6H_5)_2$	+0.06	NMR-F-B	[81]
$Si(C_6H_5)_3$	(0.00)	Ph	[106]
$Si(C_6H_5)_3$	0.0	IR-B	[107]
$Si(C_6H_5)_3$	[+0.06]	NMR-F-B	[81]
$Si(C_6H_5)_3$	+0.08	NMR-C-B	[80]
$Si(C_6H_5)_3$	+0.09	NMR-C-B	[50, 53]
$Si[N(CH_3)_2]_3$	0.0	NMR-F-B	[81]
$Si[N(CH_3)_2]_3$	+0.11	NMR-C-B	[50, 53, 80]
$Si(OH)_3$	+0.14	NMR-C-B	[53]
$Si(CH_3)(C_6H_5)(OCH_3)$	+0.10	NMR-C-B	[83]
$Si(OCH_3)_3$	[+0.08]	NMR-C-B	[52]
$Si(OCH_3)_3$	+0.11	NMR-C-B	[80]
$Si(OCH_3)_3$	+0.12	NMR-C-S1	[50]
$Si(OCH_3)_3$	+0.13	NMR-F-B	[81]
$Si(OCH_3)_3$	+0.13	NMR-C-B	[50, 53]
$Si(CH_3)(C_6H_5)(OC_2H_5)$	+0.10	NMR-C-B	[83]
$Si(OC_2H_5)_3$	[+0.08]	NMR-C-B	[52]
$Si(OC_2H_5)_3$	+0.08	IR-B	[84, 105]
$Si(OC_2H_5)_3$	+0.08	IR-E	[84]
$Si(OC_2H_5)_3$	+0.10	NMR-C-S1	[50]
$Si(OC_2H_5)_3$	+0.12	NMR-C-B	[50, 53, 80]
$Si(OC_2H_5)_3$	+0.26	IR-A	[84]
$Si(CH_3)(C_6H_5)(OC_3H_7\text{-}n)$	+0.10	NMR-C-B	[83]
$Si(OC_3H_7\text{-}n)_3$	+0.13	NMR-C-B	[80]
$Si(CH_3)C_6H_5)(OC_3H_7\text{-}iso)$	+0.09	NMR-C-B	[83]
$Si(OC_3H_7\text{-}iso)_3$	+0.08	NMR-C-B	[52]
$Si(OC_6H_7\text{-}iso)_3$	+0.11	NMR-C-B	[50, 53]
$Si(OC_4H_9\text{-}t)_3$	+0.08	NMR-C-B	[50, 53]
$Si(OC_6H_5)_3$	+0.11	NMR-C-B	[80]
$Si(OC_6H_5)_3$	+0.16	NMR-C-B	[53]
$Si(CH_3)(C_6H_5)(OC_4H_9\text{-}n)$	+0.10	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OC_4H_9\text{-}iso)$	+0.10	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OC_4H_9\text{-}s)$	+0.09	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OCH_2C_6H_5)$	+0.10	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OCH_2CH_2Cl)$	+0.10	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OCH_2C{\equiv}CH)$	+0.10	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OCH_2CH_2CN)$	+0.11	NMR-C-B	[83]
$Si(CH_3)(C_6H_5)(OCH_2CF_3)$	+0.11	NMR-C-B	[83]
$Si(OCOCH_3)_3$	+0.20	NMR-C-B	[50, 53]
$Si(OCOCF_3)_3$	+0.28	NMR-C-B	[50, 53]
$Si(CH_3)_2OSi(CH_3)_3$	+0.12	NMR-F-B	[81]
$Si[OSi(CH_3)_3]_3$	+0.10	NMR-C-B	[50, 53]
$Si(OCH_2CH_2)_3N$	0.0	NMR-C-S1	[50]
$Si(OCH_2CH_2)_3N$	[+0.02]	NMR-C-B	[50, 52, 53]
$Si(OCH_2CH_2)_3N$	+0.02	IR-B	[84]
$Si(OCH_2CH_2)_3N$	+0.05	IR-E	[84]
$Si(OCH_2CH_2)_3N$	+0.06	NMR-C-B	[80]
$Si(OCH_2CH_2)_3N$	+0.10	IR-A	[84]
$Si(OCH_2CH_2NH_2)_3$	+0.13	NMR-C-B	[50, 53]
$Si(SC_2H_5)_3$	+0.16	NMR-C-B	[53]
$Si(CH_3)_2F$	+0.11	NMR-F-B	[81]
SiF_3	(+0.17)	NMR-C-B	[80]
SiF_3	+0.23	NMR-C-B	[50, 53]
SiF_3	+0.24	NMR-F-B	[81]
SiF_3	+0.24	NMR-C-S1	[50]
$Si(CH_3)_2CH_2CH_2CF_3$	+0.06	NMR-F-B	[81*]
$Si(CH_3)_2Cl$	+0.10	NMR-F-B	[81]
$Si(CH_3)Cl_2$	+0.15	NMR- F-B	[81]
$SiCl_3$	+0.09	IR-B	[105]
$SiCl_3$	[+0.17]	NMR-C-B	[80]
$SiCl_3$	+0.19	NMR-F-B	[81*]
$SiCl_3$	+0.21	NMR-C-S1	[50]
$SiCl_3$	+0.21	NMR-C-B	[50, 53]
$Si(CH_3)_2CH_2Cl$	+0.08	NMR-F-B	[81*]
$Si(CH_3)ClBr$	+0.15	NMR-F-B	[81*]
$SiBr_3$	+0.18	NMR-F-B	[81*]
$SiBr_3$	+0.20	NMR-C-B	[80]
$SiBr_3$	+0 21	NMR-C-B	[50, 53]

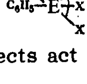
Table 3 (continued).

Substituent	σ_R^0	Method of determination	Refs.
$Si(CH_3)_2Si(CH_3)_3$	+0.04	IR-B	[102]
$Si(CH_3)[Si(CH_3)_3]_2$	+0.06	IR-B	[102]
CH_2SiH_3	+0.16	NMR-C-B	[49]
$CH_2Si(CH_3)_3$	+0.21	NMR-C-B	[88]
$CH_2Si(CH_3)_3$	+0.20	NMR-C-B	[49]
$CH_2Si(CH_3)_3$	+0.20	NMR-F-B	[16, 87, 108]
$CH_2Si(CH_3)_3$	+0.20	IR-B	[102]
$CH_2Si(CH_3)_3$	+0.19	NMR-F-N	[88]
$CH_2Si(CH_3)_3$	+0.18	NMR-C-B	[17*, 49]
$CH_2Si(CH_3)_3$	+0.17	IR-B	[109]
$CH_2Si(CH_3)_3$	(−0.15)	NMR-C-S, NMR-H-S	[57]
$CH_2SiH(C_2H_5)_2$	−0.23	IR-B	[109]
$CH_2Si(C_2H_5)_3$	−0.21	NMR-C-B	[49]
$CH_2Si(C_2H_5)_3$	−0.19	NMR-C-B	[17*, 49]
$CH_2Si(n\text{-}C_3H_7)_3$	−0.21	NMR-C-B	[49]
$CH_2Si(n\text{-}C_3H_7)_3$	−0.19	NMR-C-B	[17*, 49]
$CH_2SiH(t\text{-}C_4H_9)_2$	−0.22	IR-B	[109]
$CH_2Si(CH_3)_2C_6H_5$	−0.20	NMR-C-B	[49]
$CH_2Si(CH)_3(C_6H_5)_2$	−0.19	NMR-C-B	[49]
$CH_2Si(C_6H_5)_3$	−0.18	NMR-C-B	[49]
$CH_2Si(C_6H_5)_3$	−0.16	NMR-F-N	[88]
$CH_2Si(CH_3)_2OCH_3$	−0.19	NMR-C-B	[49]
$CH_2Si(CH_3)_2OCH_3$	−0.17	NMR-C-B	[17*, 49]
$CH_2Si(CH_3)(OCH_3)_2$	−0.18	NMR-C-B	[49]
$CH_2Si(CH_3)(OCH_3)_2$	−0.17	NMR-C-B	[17*, 49]
$CH_2Si(OCH_3)_3$	−0.18	NMR-F-B	[90]
$CH_2Si(OCH_3)_3$	−0.17	NMR-C-B	[49]
$CH_2Si(OCH_3)_3$	−0.16	NMR-C-B	[17*, 49]
$CH_2Si(OCH_2CH_2)_3N$	−0.21	NMR-F-B	[90]
$CH_2SiH(CH_3)(CH_2C_6H_5)$	−0.21	IR-B	[109]
$CH_2SiH(C_2H_5)(CH_2C_6H_5)$	−0.22	IR-B	[109]
$CH_2Si(CH_3)(CH_2C_6H_5)_2$	−0.24	IR-B	[109]
$CH[Si(CH_3)_3]_2$	−0.24	IR-B	[102]
$CH[Si(CH_3)_3]_2$	−0.22	NMR-C-B	[49]
$C[Si(CH_3)_3]_3$	−0.22	NMR-C-B	[49]
$COOCH_2Si(OC_2H_5)_3$	+0.22	NMR-C-B	[92]
$COOCH_2Si(OCH_2CH_2)_3N$	+0.20	NMR-C-B	[92]
$COOCH_2SiF_3$	+0.22	NMR-C-B	[92]
$NHSi(CH_3)_3$	−0.78	NMR-C-B	[93]
$OSi(CH_3)_3$	−0.53	NMR-C-B	[93]
$OSi(CH_3)_3$	−0.48	IR-B	[110]

Notation: IR-B—analysis of the intensities of the *A* absorption band in the region of 1600 cm^{-1} in the IR spectra of monosubstituted benzenes using the relation $\sigma_R^0 = 0.0075 (A-100)^{1/2}$; [32,33,60] NMR-C-S1—analysis of the chemical shifts in the ^{13}C NMR spectra of the β-substituted styrenes $C_6H_5CH{=}CHX$; [50] IR-HB-A—IR spectroscopic study of the hydrogen bond formed by acetylene derivatives with phenol; [63] IR-E—analysis of the intensity of the *A* stretching vibration band of the double bond in the IR spectra of monosubstituted ethylenes using the relation $\sigma_R^0 = 0.0060 (A-80)^{1/2}$; [60] IR-A—analysis of the intensity of the *A* stretching vibration band of the triple bond in the IR spectra of monosubstituted acetylenes using the relation $\sigma_R^0 = 0.0046 A^{1/2} - 0.05$; [60] for the significance of the remaining designations of the methods, see the footnote to Table 1.

In this respect, the groups EX_3 resemble organic substituents for which the values of σ_R are likewise not invariant; when the electronic characteristics of the reaction centre are changed significantly, the sign of the constants may also change.[112] The condition that the fragment D is invariant holds for the majority of studies in which the σ_R^0 constants have been obtained for the substituents EX_3. These constants have been determined mainly for benzene derivatives. Almost all the values of σ_R^0 presented in Tables 3 and 4 characterise the resonance properties of the substituents EX_3 in relation to the benzene ring ($D = C_6H_5$). (See below, for the acetylene derivatives).

Another feature of the constants σ_R^0 (Tables 3 and 4) is that their values reflect not only the effects due to the (p–d)π interaction but also the σ, π conjugation



$C_6H_5{-}EX_3$ [113].

These two resonance effects act in opposite directions.

Table 4. The constants σ_R^0 of germanium-, tin-, and lead-containing substituents.

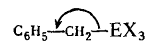
Substituent	σ_R^0	Method of determination	Refs.
$Ge(CH_3)_3$	(−0.1)	Ph	[106]
$Ge(CH_3)_3$	−0.06	IR-HB-A	[63*]
$Ge(CH_3)_3$	+0.01	NMR-F-N	[46]
$Ge(CH_3)_3$	+0.01	NMR-F-B	[46, 104, 108]
$Ge(CH_3)_3$	+0.05	IR-B	[102]
$Ge(CH_3)_3$	(+0.07)	NMR-C-S, NMR-H-S	[57]
$Ge(C_2H_5)_3$	−0.07	IR-HB-A	[63*]
$Ge(C_2H_5)_3$	0.0	IR-B	[107]
$Ge(C_6H_5)_3$	0.0	Ph	[106]
$Ge(OCH_3)_3$	∼+0.14	NMR-C-B	[51]
$Ge(OC_2H_5)_3$	∼+0.14	NMR-C-B	[51]
$Ge(OC_3H_7\text{-}iso)_3$	∼+0.13	NMR-C-B	[51]
$Ge(OC_4H_9\text{-}t)_3$	∼+0.10	NMR-C-B	[51]
$Ge(OCH_2CH_2)_3N$	∼+0.05	NMR-C-B	[51]
GeF_3	+0.23	NMR-F-B	[94]
$GeCl_3$	+0.16	NMR-F-B	[94]
$GeBr_3$	+0.14	NMR-F-B	[94]
$CH_2Ge(CH_3)_3$	−0.23	IR-B	[109]
$CH_2Ge(CH_3)_3$	−0.21	NMR-C-B	[88]
$CH_2Ge(CH_3)_3$	−0.20	NMR-F-N	[88]
$CH_2Ge(CH_3)_3$	(−0.15)	NMR-C-S, NMR-H-S	[57]
$CH_2GeH_2C_2H_5$	−0.24	IR-B	[109]
$CH_2Ge(C_2H_5)_3$	−0.21	NMR-C-B	[49]
$CH_2Ge(C_6H_5)_3$	−0.17	NMR-F-N	[88]
$CH_2Ge(OC_2H_5)_3$	−0.24	IR-B	[109]
$CH_2GeH_2(CH_2C_6H_5)$	−0.23	IR-B	[109]
$CH_2GeH(C_2H_5)(CH_2C_6H_5)$	−0.24	IR-B	[109]
$CH_2GeH(CH_2C_6H_5)_2$	−0.24	IR-B	[109]
$Sn(CH_3)_3$	−0.13	IR-HB-A	[63*]
$Sn(CH_3)_3$	−0.02	NMR-F-N	[46]
$Sn(CH_3)_3$	0.0	IR-E	[105]
$Sn(CH_3)_3$	[+0.01]	NMR-F-B	[46, 95, 104, 105, 108]
$Sn(CH_3)_3$	+0.05	NMR-C-S, NMR-H-S	[57]
$Sn(CH_3)_3$	+0.07	IR-B	[102]
$Sn(C_2H_5)_3$	+0.01	NMR-F-B	[95]
$Sn(n\text{-}C_4H_9)_3$	0.00	NMR-F-B	[95]
$Sn(CH{=}CH_2)_3$	0.00	IR-E	[105]
$Sn(C_6H_5)_3$	0.0	Ph	[106]
$Sn(C_6H_5)_3$	0.0	IR-B	[107]
$Sn(C_6H_5)_3$	+0.03	NMR-F-B	[95, 97, 99]
$Sn(C_6H_4F\text{-}4)_3$	+0.03	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	+0.04	NMR-F-B	[95]
$SnCl_3$	+0.15 ($CDCl_3$)	NMR-F-B	[95]
$SnCl_3$	+0.07 ($(CD_3)_2CO$)	NMR-F-B	[95]
$SnCl_3$	+0.14 (CCl_4)	NMR-F-B	[95]
$CH_2Sn(CH_3)_3$	−0.26	IR-B	[102]
$CH_2Sn(CH_3)_3$	−0.25	NMR-F-N	[88]
$CH_2Sn(CH_3)_3$	−0.25	NMR-C-B	[88]
$CH_2Sn(CH_3)_3$	−0.24	NMR-C-N	[88]
$CH_2Sn(CH_3)_3$	−0.23	NMR-F-B	[108]
$CH_2Sn(CH_3)_3$	(−0.19)	NMR-C-S, NMR-H-S	[57]
$CH_2Sn(C_6H_5)_3$	−0.22	NMR-F-N	[88]
$CH_2Sn(C_6H_5)_3$	−0.21	NMR-F-B	[96, 97, 99]
$OSn(C_2H_5)_3$	−0.48	NMR-F-B	[98]
$OSn(C_6H_5)_3$	−0.45	NMR-F-B	[98]
$SSn(C_2H_5)_3$	−0.17	NMR-F-B	[101]
$SSn(C_6H_5)_3$	−0.14	NMR-F-B	[97, 99]
$Pb(CH_3)_3$	−0.08	NMR-F-N	[46]
$Pb(CH_3)_3$	[−0.02]	NMR-F-B	[46]
$Pb(CH_3)_3$	+0.05	NMR-C-S, NMR-H-S	[57]
$Pb(C_6H_5)_3$	−0.01	NMR-F-B	[99]
$Pb(C_6H_5)_3$	0.0	Ph	[106]
$Pb(C_6H_5)_3$	(0.0)	IR-B	[107]
$CH_2Pb(CH_3)_3$	−0.25	NMR-C-B	[88]
$CH_2Pb(CH_3)_3$	−0.25	NMR-F-N	[88]
$CH_2Pb(CH_3)_3$	−0.24	NMR-C-N	[88]
$CH_2Pb(CH_3)_3$	(−0.19)	NMR-C-S, NMR-H-S	[57]
$CH_2Pb(C_6H_5)_3$	−0.21	NMR-F-N	[88]
$CH_2Pb(C_6H_5)_3$	−0.19	NMR-F-B	[96, 99]
$OPb(C_6H_5)_3$	−0.46	NMR-F-B	[97, 99]
$SPb(C_6H_5)_3$	−0.11	NMR-F-B	[97, 99]

Notation: NMR-C-N—analysis of the chemical shifts in the ^{13}C NMR spectra of naphthalene derivatives; [58] for the significance of the remaining designations of the methods, see the footnotes to Tables 1 and 3.
Note: The solvents are indicated in brackets.

Although a series of quantum-chemical[113–115] and experimental[44,88,116] studies have been devoted to the characteristics of σ, π conjugation, there are many unsolved problems as regards the estimation of the relative contributions of the (p–d)π interaction and the σ, π conjugation to the overall resonance effect of EX_3 relative to the benzene ring. Some of these will be considered below in the analysis of the σ_p

and σ_p^+ constants of EX$_3$. Here we may note that the $(p-d)\pi$ interaction is weakened as the atomic number of E increases, while the σ,π conjugation actually becomes more intense. Therefore, for isostructural compounds, the contribution of the $(p-d)\pi$ interaction to the overall resonance effect of EX$_3$ relative to the aromatic ring is most significant when E = Si and the contribution of the σ,π conjugation is greatest when E = Pb. The stronger σ,π conjugation in acetylene derivatives[44,63] leads to negative values of σ_R^0 for E = Ge, Sn and to low values of σ_p (see below) for EX$_3$ linked by a triple bond.

As noted above, the constants σ_R^0 of the substituents EX$_3$ in CH$_2$EX$_3$ have different signs. The negative signs of the constants σ_R^0 for the groups CH$_2$EX$_3$ are due to the σ,π conjugation in benzyl derivatives:


$C_6H_5-CH_2-EX_3$

There is no effect of the $(p-d)\pi$ interaction in these compounds.

We may note certain features in the way the constants σ_R^0 of the substituents EX$_3$ vary as a function of the nature of E and X. For the substituents E(CH$_3$)$_3$, the constants σ_R^0 decrease with increase of the atomic number of E, which corresponds to the maximum degree of the $(p-d)\pi$ interaction in silicon compounds. The low values of σ_R^0 for the substituents PbAlk$_3$ are caused by the maximum degree of the σ,π conjugation and the minimum degree of the $(p-d)\pi$ interaction for lead compounds. For constant E, the enhancement of the electron-accepting properties of X and EX$_3$ increases the effective positive charge on E and intensifies the resonance electron-accepting properties of the substituents EX$_3$ (i.e. increases their σ_R^0 constants) for the following sequence of X: Alk < AlkO < Hal. For the same reason, the constants σ_R^0 increase with increase of n in the groups E(CH$_3$)$_{3-n}$Hal. The constants σ_R^0 of the substituents CH$_2$EX$_3$ show a tendency to decrease following the enhancement of the electron-accepting properties of X and to increase with increase of the atomic number of E, i.e. with increase of the polarisability of the E–C bonds.

Table 5. The constants σ_m and σ_p of silicon-containing substituents.

Substituent	σ_m	σ_p	Method of determination	Refs.
SiH$_3$	—	+0.07	DM	[68]
SiH$_3$	+0.05	+0.10	NMR-F-B	[81]
SiH$_3$	—	+0.10	Ph	[68]
SiH(CH$_3$)$_2$	+0.01	+0.04	Ph	[81]
SiH(CH$_3$)$_2$	—	−0.05	DM	[68]
SiH(CH$_3$)$_2$	—	+0.06	Ph	[68]
Si(CH$_3$)$_3$	—	−0.11	IR-HB-A	[63]
Si(CH$_3$)$_3$	—	[−0.10]	Ph	[116]
Si(CH$_3$)$_3$	−0.09	−0.07	Ph, X	[103]
Si(CH$_3$)$_3$	−0.04	−0.07	X-1	[69]
Si(CH$_3$)$_3$	−0.21	−0.06	X-1	[71]
Si(CH$_3$)$_3$	—	−0.05	DM	[68]
Si(CH$_3$)$_3$	0.00	−0.05	X-5	[74]
Si(CH$_3$)$_3$	0.00	−0.03	Ph, X-1, X-4	[70]
Si(CH$_3$)$_3$	+0.02	0.00	X-4	[72]
Si(CH$_3$)$_3$	+0.11	0.00	X-1	[117]
Si(CH$_3$)$_3$	−0.04	+0.03	X	[72]
Si(CH$_3$)$_3$	—	+0.06	Ph	[68]
Si(CH$_3$)$_3$	−0.08	+0.07	X	[69]
Si(CH$_3$)$_3$	−0.03	+0.08	X-3	[69]
Si(CH$_3$)$_3$	−0.02	(+0.11)	X-3	[69]
Si(C$_2$H$_5$)$_3$	—	−0.14	IR-HB-A	[63]
Si(C$_2$H$_5$)$_3$	—	0.0±0.1	X-1	[14]
Si(CH$_3$)$_2$C$_6$H$_5$	+0.04	+0.07	NMR-F-B	[81]
Si(CH$_3$)(C$_6$H$_5$)$_2$	+0.10	+0.13	NMR-F-B	[81]
Si(C$_6$H$_5$)$_3$	—	[−0.08]	NMR-C-B	[53]
Si(C$_6$H$_5$)$_3$	−0.03	+0.09	X	[73]
Si(C$_6$H$_5$)$_3$	−0.03	+0.10	X-4	[73]

Table 5 (continued).

Substituent	σ_m	σ_p	Method of determination	Refs.
Si(C$_6$H$_5$)$_3$	+0.16	+0.19	NMR-F-B	[81]
Si(C$_6$H$_5$)$_3$	+0.12	+0.27	X	[73]
Si(C$_6$H$_5$)$_3$	+0.08	(+0.31)	X	[73]
Si[N(CH$_3$)$_2$]$_3$	−0.04	−0.04	NMR-F-B	[81]
Si[N(CH$_3$)$_2$]$_3$	—	+0.05	DM	[68]
Si(CH$_3$)$_2$OCH$_3$	+0.04	(−0.02)	X-5	[74]
Si(CH$_3$)$_2$OCH$_3$	—	+0.10	Ph	[68]
Si(CH$_3$)$_2$OCH$_3$	—	+0.12	DM	[68]
Si(CH$_3$)(OCH$_3$)$_2$	+0.04	(+0.01)	X-5	[74]
Si(CH$_3$)(OCH$_3$)$_2$	—	+0.15	Ph	[68]
Si(CH$_3$)(OCH$_3$)$_2$	—	+0.18	DM	[68]
Si(OCH$_3$)$_3$	—	+0.10	Ph	[68]
Si(OCH$_3$)$_3$	+0.06	+0.13	NMR-F-B	[81]
Si(OCH$_3$)$_3$	+0.09	+0.13	X-5	[74]
Si(OCH$_3$)$_3$	—	+0.19	DM	[68]
Si(OC$_2$H$_5$)$_3$	—	−0.01	Ph	[53]
Si(OC$_2$H$_5$)$_3$	+0.02	+0.08	NMR-F-B	[81]
Si(CH$_3$)$_2$OSi(CH$_3$)$_3$	−0.01	0.00	Ph, X-1, X-4	[70]
Si(CH$_3$)[OSi(CH$_3$)$_3$]$_2$	−0.03	+0.01	Ph, X-1, X-4	[70]
Si[OSi(CH$_3$)$_3$]$_3$	−0.06	+0.02	Ph, X-1, X-4	[70]
Si(CH$_3$)$_2$F	—	+0.15	Ph	[68]
Si(CH$_3$)$_2$F	+0.12	+0.16	Ph, X-1, X-4	[70]
Si(CH$_3$)$_2$F	—	+0.17	X-5	[74]
Si(CH$_3$)$_2$F	+0.13	+0.19	NMR-F-B	[81]
Si(CH$_3$)$_2$F	—	+0.23	DM	[68]
Si(CH$_3$)F$_2$	—	+0.23	X-5	[74]
Si(CH$_3$)F$_2$	—	+0.28	Ph	[68]
Si(CH$_3$)F$_2$	—	+0.40	DM	[68]
Si(CH$_3$)F$_2$	—	[+0.42]	X, Ph	[116]
Si(CH$_3$)F$_2$	+0.29	—	Ph, X-1, X-4	[70]
SiF$_3$	—	(+0.01)	X-5	[74]
SiF$_3$	—	+0.51	DM, Ph	[68]
SiF$_3$	+0.54	[+0.66]	Ph	[95]
SiH$_2$Cl	—	+0.26	X, Ph	[116]
Si(CH$_3$)$_2$Cl	+0.07	+0.02	X-5	[74]
Si(CH$_3$)$_2$Cl	—	+0.15	Ph	[68]
Si(CH$_3$)$_2$Cl	+0.16	[+0.21]	NMR-F-B	[81]
Si(CH$_3$)$_2$Cl	—	+0.30	DM	[68]
Si(CH$_3$)Cl$_2$	+0.09	[+0.08]	X-5	[74]
Si(CH$_3$)Cl$_2$	+0.31	[+0.39]	NMR-F-B	[81]
Si(CH$_3$)Cl$_2$	—	+0.41	DM	[68]
Si(CH$_3$)Cl$_2$	—	+0.42	Ph	[68]
SiCl$_3$	+0.19	(+0.20)	X-5	[74]
SiCl$_3$	—	+0.37	Ph	[68]
SiCl$_3$	—	+0.43	DM	[68]
SiCl$_3$	+0.48	[+0.56]	Ph	[94]
Si(CH$_3$)$_2$Br	—	+0.10	X-5	[74]
Si(CH$_3$)Br$_2$	—	+0.30	X-5	[74]
SiBr$_3$	—	(+0.27)	DM	[68]
SiBr$_3$	—	+0.41	X-5	[74]
SiBr$_3$	+0.48	[+0.57]	Ph	[94]
CH$_2$Si(CH$_3$)$_3$	−0.16	−0.21	X-1	[14]
CH$_2$Si(CH$_3$)$_3$	−0.20	−0.26	X-1, X-3	[118]
CH$_2$Si(CH$_3$)$_3$	−0.17	−0.27	X	[16, 31]
CH$_2$Si(C$_2$H$_5$)$_3$	—	−0.24	X-1, X-3	[118]
CH$_2$CH$_2$Si(CH$_3$)$_3$	—	−0.17	X-1, X-3	[118]
CH$_2$CH$_2$Si(C$_2$H$_5$)$_3$	—	−0.14	X-1, X-3	[118]
CH$_2$OSi(CH$_3$)$_3$	—	−0.05	Ph, X-1, X-5	[70]

Notation: DM—on the basis of the linear relation between the dipole moments of *para*-substituted toluenes and the σ_p constants of the substituents;[68] X-3—the study of the pK of substituted anilines;[69] X-4—the study of the rate constants for the reactions of substituted benzoic acids with diphenyldiazomethane:[70–73] X-5—the study of the rate constants for the bromination of substituted dimethylphenylsilanes;[74] for the significance of the remaining designations of the methods, see the footnotes to Tables 1 and 3.

3. The Hammett Constants σ_p and σ_m

These constants characterise quantitatively the overall electronic effect (inductive and resonance) of the substituents EX$_3$. Approximate values of σ_p can be obtained, using the relation $\sigma_p = \sigma_I + \sigma_R$, from the approximate estimate $\sigma_m \cong \sigma_I$; the difficulties arising in this procedure have been described.[11] In interpreting the constants σ_p, one should bear in mind the problems discussed in the analysis of the constants σ_I and σ_R^0. Furthermore, a considerable proportion of the constants σ_m and σ_p have been determined by chemical methods (Tables 5 and 6), which might have led to the appearance of appreciable non-controllable errors. Therefore, a non-critical application of these constants entails inevitably large errors and it is difficult to avoid subjectivity in estimating the most and least reliable values of the constants.

Table 6. The constants σ_m and σ_p of germanium, tin-, and lead-containing substituents.

Substituent	σ_m	σ_p	Method of determination	Refs.
GeH_3	—	+0.01	DM	[68]
$Ge(CH_3)_3$	—	−0.18	IR-HB-A	[63]
$Ge(CH_3)_3$	—	[−0.06]	X, Ph	[116]
$Ge(CH_3)_3$	—	−0.06	DM	[68]
$Ge(CH_3)_3$	0,00	0.00	X-1	[14]
$Ge(CH_3)_3$	—	+0.01	Ph	[68]
$Ge(C_2H_5)_3$	—	−0.20	IR-HB-A	[63]
$Ge(C_2H_5)_3$	0.00	0.00	X-1	[14]
$Ge(C_2H_5)_3$	—	0.0±0.1	X-1	[14]
$Ge(C_6H_5)_3$	+0.05	+0.08	X-4	[73]
$Ge(C_6H_5)_3$	—	[+0.16]	X, Ph	[116]
$Ge(C_6H_5)_3$	+0.15	+0.24	X	[69]
$GeH(C_6H_5)_2$	—	+0.16	X, Ph	[116]
GeF_3	+0.85	+0.97	Ph	[94]
$GeCl_3$	—	+0.60	DM, Ph	[68]
$GeCl_3$	+0.71	[+0.79]	Ph	[94]
$Ge(C_6H_5)_2Br$	—	+0.35	X, Ph	[116]
$Ge(C_6H_5)Br_2$	—	+0.60	X, Ph	[116]
$GeBr_3$	+0.66	+0.73	Ph	[94]
$Sn(CH_3)_3$	—	−0.26	IR-HB-A	[63]
$Sn(CH_3)_3$	—	[−0,12]	X, Ph	[116]
$Sn(CH_3)_3$	—	0.0±0.1	X-1	[14]
$Sn(CH_3)_3$	—	+0.02	NMR-F-B	[95]
$Sn(C_2H_5)_3$	—	0,0±0.1	X-1	[14]
$Sn(C_2H_5)_3$	—	+0.03	NMR-F-B	[95]
$Sn(\text{н-}C_4H_9)_3$	—	+0.02	NMR-F-B	[95]
$Sn(C_6H_5)_3$	—	+0.18 ($CDCl_3$)	NMR-F-B	[95, 99]
$Sn(C_6H_5)_3$	—	+0.23 $(CD_3)_2CO$	NMR-F-B	[95]
$Sn(C_6H_5)_3$	—	+0.21 (CCl_4)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}4)_3$	—	+0.29 ($CDCl_3$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}4)_3$	—	+0.28 ($(CD_3)_2CO$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}4)_3$	—	+0.32 (CCl_4)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	—	+0.32 ($CDCl_3$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	—	+0.30 ($(CD_3)_2CO$)	NMR-F-B	[95]
$Sn(C_6H_4F\text{-}3)_3$	—	+0.36 (CCl_4)	NMR-F-B	[95]
$SnH(C_6H_5)_2$	—	+0.20	Ph	[116]
$Sn(C_6H_5)_2Cl$	—	+0.40	Ph	[116]
$SnCl_3$	—	+0.97 ($CDCl_3$)	NMR-F-B	[95]
$SnCl_3$	—	+0.49 ($(CD_3)_2CO$)	NMR-F-B	[95]
$SnCl_3$	—	+0.94 (CCl_4)	NMR-F-B	[95]
$Pb(C_6H_5)_3$	—	+0.21	NMR-F-B	[99]

Note: The solvents are indicated in brackets; for the significance of the designations of the methods, see the footnotes to Tables 1, 3, and 5.

However, one should note that the constants σ_p and σ_m carry nevertheless important qualitative information about the electronic effects of EX_3. Thus the constants σ_p for $E(CH_3)_3$ are larger (−0.06– −0.13) than for the group $C(CH_3)_3$ (−0.20[11]). These estimates show that the resonance electron-accepting properties of organoelemental substituents must be more significant. The above conclusion has also been confirmed by the fact that the constants σ_p are larger than σ_m. The higher values of the constants σ_p for the substituents EX_3 than the corresponding values of σ_m are due to the presence in the former of a considerable resonance component, which is always positive. When this resonance component is negative, then $\sigma_p < \sigma_m$, which has in fact been observed for the substituent $CH_2Si(CH_3)_3$. It was noted above that, following the enhancement of the electron-accepting properties of X and EX_3, the constants σ_I and σ_R^0 increase; naturally, this also entails an increase of the constants σ_p.

Table 7. The constants σ_p^+ of silicon-containing substituents.

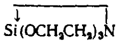
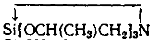
Substituent	σ_p^+	Method of determination	Refs.
SiH_3	[−0.01]	UV-2	[119*]
SiH_3	+0.03	UV-3	[119*]
$SiH(CH_3)_2$	−0,16	UV-3	[120*]
$SiH(CH_3)_2$	−0.14	UV-2	[120*]
$Si(CH_3)_3$	[−0.22]	UV-1	[121]
$Si(CH_3)_3$	−0.15	UV-3	[120*]
$Si(CH_3)_3$	−0.14	IP	[114*]
$Si(CH_3)_3$	[−0.13]	UV-2	[120*]
$Si(CH_3)_3$	−0,03	X	[122]
$Si(CH_3)_3$	0.0	NMR-H-P	[59]
$Si(CH_3)_3$	[+0.02]	X	[15]
$Si(C_2H_5)_3$	−0.16	UV-3	[119*]
$Si(C_2H_5)_3$	−0.14	UV-2	[119*]
$Si(n\text{-}C_4H_9)_3$	−0.18	UV-3	[120*]
$Si(n\text{-}C_4H_9)_3$	−0.16	UV-2	[120*]
$Si(t\text{-}C_4H_9)_3$	−0.18	UV-3	[119*]
$Si(t\text{-}C_4H_9)_3$	−0.16	UV-3	[119*]
$SiH_2C_6H_5$	−0,02	UV-2	[119*]
$SiH_2C_6H_5$	~0	UV-3	[119*]
$SiH_2C_6H_5$	~0	IP	[123*]
$SiH(CH_3)(C_6H_5)$	−0,06	UV-2	[120*]
$SiH(CH_3)(C_6H_5)$	−0,05	UV-3	[120*]
$SiH(C_2H_5)(C_6H_5)$	−0.06	UV-2	[120*]
$SiH(C_2H_5)(C_6H_5)$	−0.05	UV-3	[120*]
$Si(CH_3)_2C_6H_5$	−0.09	UV-2	[119*]
$Si(CH_3)_2C_6H_5$	−0,09	UV-3	[119*]
$SiH(C_6H_5)_2$	−0.09	IP	[123*]
$SiH(C_6H_5)_2$	−0.01	UV-2	[119*]
$SiH(C_6H_5)_2$	+0.01	UV-3	[119*]
$Si(CH_3)(C_6H_5)_2$	−0.05	UV-2	[119*]
$Si(CH_3)(C_6H_5)_2$	−0.04	UV-3	[119*]
$Si(C_2H_5)(C_6H_5)_2$	−0.06	UV-2	[120*]
$Si(C_2H_5)(C_6H_5)_2$	−0 05	UV-3	[120*]
$Si(C_6H_5)_3$	−0.18	UV-3	[119*]
$Si(C_6H_5)_3$	−0.15	UV-2	[119*]
$Si(C_6H_5)_2OH$	−0.04	UV-2	[120*]
$Gi(C_6H_5)_2OH$	−0.03	UV-3	[120*]
$Si(OC_2H_5)_3$	+0.01	UV-2	[124*]
 $Si(OCH_2CH_2)_3N$	−0.21	UV-2	[90*]
 $Si[OCH(CH_3)CH_2]_3N$	−0.24	UV-2	[90*]
$Si(CH_3)F_2$	+0.37	IP	[125*]
SiF_3	~+0.7	IP	[125*]
SiH_2Cl	[+0.09]	UV-2	[119*]
SiH_2Cl	+0.16	UV-3	[119*]
$Si(CH_3)_2Ci$	+0.05	UV-2	[116]
$Si(CH_3)_2Cl$	+0.05	IP	[125*]
$Si(CH_3)Cl_2$	[+0,13]	UV-2	[120*]
$Si(CH_3)Cl_2$	+0.21	IP	[125*]
$Si(CH_3)Cl_2$	+0.22	UV-3	[120*]
$SiCl_3$	[+0.16]	UV-2	[120*]
$SiCl_3$	+0.24	IP	[125*]
$SiCl_3$	+0.26	UV-3	[120*]
$SiH_2(CH_2Cl)$	−0,04	UV-2	[120*]
$SiH_2(CH_2Cl)$	−0.03	UV-3	[120*]
$Si(CH_3)_2Si(CH_3)_3$	−0.62	UV-1	[121]
$Si(CH_3)_2Si(CH_3)_3$	[−0.55]	UV-2	[67, 121*]]
$Si(CH_3)_2Si(CH_3)_3$	−0 23	NMR-H-P	[59]
$1\text{-}Si_3(CH_3)_7$	−0.77	UV-1	[121]
$1\text{-}Si_3(CH_3)_7$	[−0,67]	UV-2	[67, 121*]
$2\text{-}Si_3(CH_3)_7$	−0.81	UV-1	[121]
$2\text{-}Si_3(CH_3)_7$	[−0.70]	UV-2	[67, 121*]
CH_2SiH_3	−0,27	UV-2	[49]
CH_2SiH_3	−0,15	UV-2	[124*]
$CH_2Si(CH_3)_3$	[−0,66]	UV-1	[121]
$CH_2Si(CH_3)_3$	−0.66; −0.63	UV-1	[65]
$CH_2Si(CH_3)_3$	−0,63	IP	[114*]
$CH_2Si(CH_3)_3$	−0.62	UV-1	[126]
$CH_2Si(CH_3)_3$	−0,61	X	[65]
$CH_2Si(CH_3)_3$	−0.56	X	[49]
$CH_2Si(CH_3)_3$	−0,55	UV-2	[67][a]
$CH_2Si(CH_3)_3$	−0.50	UV-2	[119*]
$CH_2Si(CH_3)_3$	−0,54	X	[130]
$CH_2Si(CH_3)_3$	−0,54	UV-2	[49]
$CH_2Si(CH_3)_3$	[−0,54±0,01]	UV-2	[67][b]
$CH_2Si(CH_3)_3$	−0.4	NMR-C-B	[55]
$CH_2SiH(C_2H_5)_2$	−0.55	UV-2	[109*]
$CH_2Si(C_2H_5)_3$	−0,57	X	[49]
$CH_2Si(C_2H_5)_3$	−0.57	UV-2	[49]
$CH_2SiH_2(n\text{-}C_3H_7)$	−0.57	UV-2	[67, 120*]
$CH_2Si(n\text{-}C_3H_7)_3$	−0.58	UV-2	[49]
$CH_2Si(n\text{-}C_3H_7)_3$	−0.57	X	[49]
$CH_2Si(n\text{-}C_4H_9)_3$	−0.55	UV-2	[67, 120*]
$CH_2SiH(t\text{-}C_4H_9)_2$	−0.49	UV-2	[109*]
$CH_2Si(t\text{-}C_4H_9)_3$	−0.54	UV-2	[119*]
$CH_2Si(C_6H_5)_3$	−0.42	UV-1	[66]
$CH_2Si(C_6H_5)_3$	−0.4	UV-1	[126]
$CH_2Si(C_6H_5)_3$	[−0.38±0.02]	UV-2	[67][b]
$CH_2Si(C_6H_5)_3$	−0.36	UV-2	[67][a]
$CH_2Si(CH_3)_2OCH_3$	−0.45	UV-2	[49]
$CH_2Si(CH_3)(OCH_3)_2$	−0.40	UV-2	[49]
$CH_2Si(OCH_3)_3$	−0.24	UV-2	[49]
$CH_2Si(OCH_3)_3$	−0.14	UV-2	[90*]
$CH_2Si(OC_2H_5)_3$	−0.19	UV-2	[124*]
 $CH_2Si(OCH_2CH_2)_3N$	−0.49	UV-2	[90*]

Table 7 (continued).

Substituent	σ_p^+	Method of determination	Refs.
$CH_2SiH(CH_3)(CH_2C_6H_5)$	−0,57	UV-2	[109*]
$CH_2Si(CH_3)_2(CH_2C_6H_5)$	−0,56	UV-2	[67, 120*]
$CH_2SiH(C_2H_5)(CH_2C_6H_5)$	−0.54	UV-2	[109*]
$CH_2SiH(CH_2C_6H_5)_2$	−0.45	UV-2	[67, 120*]
$CH_2Si(CH_3)(CH_2C_6H_5)_2$	−0.56	UV-2	[120*]
$CH_2Si(CH_3)_2Si(CH_3)_3$	−0.72	UV-1	[121]
$CH_2Si(CH_3)_2Si(CH_3)_3$	−0.62	UV-2	[67, 121*]
$CH[Si(CH_3)_3]_2$	(−1.06)	UV-2	[67, 131*]
$CH[Si(CH_3)_3]_2$	−0,76	UV-1	[121]
$CH[Si(CH_3)_3]_2$	[−0.65]	UV-2	[67, 121*]
$CH[Si(CH_3)_3]_2$	−0.62	X	[130]
$C[Si(CH_3)_3]_3$	(−0.79)	UV-1	[121]
$C[Si(CH_3)_3]_3$	[−0.68]	UV-2	[67, 121*]
$C[Si(CH_3)_3]_3$	−0.62	UV-2	[49]
$C[Si(CH_3)_3]_3$	(−0.52)	X	[130]
CH_2SiF_3	−0.03	UV-2	[124*]
CH_2SiCl_3	−0.08	UV-2	[124*]

Notation: UV-1—analysis of the frequency ν_{CT} of the charge-transfer bands in the UV spectra of the CTC of monosubstituted benzenes with tetracyanoethylene using the relation $\nu_{CT} = 9300\,\sigma^+ + 26\,200$;[65,66] UV-2—the same method as UV-1 but using the relation $\sigma^+ = 9.46 \times 10^{-5}\nu_{CT} - 2.466$;[67] UV-3—the same method as UV-1 but using the relation $\nu_{CT} = 7600\,\sigma^+ + 25\,800$;[38] IP—on the basis of the ionisation potentials (IP) of monosubstituted benzenes using the relation $IP = 1.31\,\sigma^+ + 9.24$;[66] NMR-H-P—analysis of the chemical shifts of the signals of the OH group in ^1H NMR spectra of phenol derivatives;[59] for the significance of the remaining designations of the methods, see the footnote to Table 1.

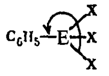
[a] Taking into account the data in Refs.65 and 127–129.

[b] Taking into account the data in Refs.65, 113, 131, and 132.

4. The Electrophilic Constants σ_p^+

The constants σ_p^+ reflect the overall influence of the electronic structure of the substituents EX_3 or CH_2EX_3 on the electron-deficient reaction centre. For the majority of the systems investigated hitherto (Tables 7 and 8), such a centre is the benzene ring, which has a positive charge. Analysis of the values of these constants constitutes an even more complex task than the interpretation of the Hammett constants σ_p. At first sight, it may turn out that there is altogether no correspondence between the values of the constants σ_p and σ_p^+ for organoelemental substituents (in contrast to organic substituents). For example, it is known[19] that, in the presence of a positive charge on the benzene ring, the p,π conjugation of the electron-donating organic substituents of the $+M$ type with the ring intensifies (the constants σ_p^+ and σ_p are negative and $\sigma_p^+ > \sigma_p$), while the conjugation remains unchanged for the electron-accepting substituents of the $-M$ type (the constants σ_p^+ and σ_p are positive and $\sigma_p^+ \cong \sigma_p$).

The values of σ_p^+ found for organoelemental compounds show that any groups EX_3 should exhibit stronger electron-donating properties (or weaker electron-accepting properties) than would follow from the estimates based on the σ_p constants. This is caused by the enhancement of the σ,π conjugation



when a positive charge arises on the ring.[116] [The second resonance effect—the $(p-d)\pi$ interaction—hardly depends on the charge on the ring.]

Table 8. The constants σ_p^+ of germanium-, tin-, and lead-containing substituents.

Substituent	σ_p^+	Method of determination	Refs.
GeH_3	−0.04	UV-2	[119*]
GeH_3	−0.03	UV-3	[119*]
$Ge(CH_3)_3$	−0.21	UV-2	[116]
$Ge(CH_3)_3$	−0.19	IP	[114*]
$Ge(CH{=}CHC_4H_9)_3$	−0.12	UV-3	[116]
$Ge(CH{=}CHC_4H_9)_3$	−0.11	UV-2	[116]
$GeH_2(C_6H_5)$	−0.04	UV-2	[120*]
$GeH_2(C_6H_5)$	−0.03	UV-3	[120*]
$Ge(CH_3)_2C_6H_5$	−0.17	UV-3	[120*]
$Ge(CH_3)_2C_6H_5$	−0 15	UV-2	[120*]
$Ge(n\text{-}C_6H_{13})_2C_6H_5$	−0.13	UV-3	[109*]
$Ge(n\text{-}C_6H_{13})_2C_6H_5$	−0.12	UV-2	[109*]
$GeH(C_6H_5)_2$	−0.07	IP	[123*]
$Ge(n\text{-}C_6H_{13})(C_6H_5)_2$	−0.12	UV-3	[109*]
$Ge(n\text{-}C_6H_{13})(C_6H_5)_2$	−0.11	UV-2	[109*]
$Ge(C_6H_5)_2CH_2CH{=}CHCH_3$	−0.11	UV-3	[109*]
$Ge(C_6H_5)_2CH_2CH{=}CHCH_3$	−0.10	UV-2	[109*]
$Ge(C_6H_5)_3$	−0.07	UV-2	[133*]
$GeH(n\text{-}C_6H_{13})Cl$	−0,06	UV-2	[109*]
$GeH(n\text{-}C_6H_{13})Cl$	−0.05	UV-3	[109*]
$GeH(C_6H_5)Cl$	−0.05	UV-2	[109*]
$GeH(C_6H_5)Cl$	−0.04	UV-3	[109*]
$GeCl_3$	+0.33	UV-2	[116]
$Ge(C_6H_5)_2Br$	−0.05	IP	[116,123*]
$Ge(C_6H_5)Br_2$	+0.09	UV-2	[116]
$Ge(C_6H_5)_2Ge(C_6H_5)_3$	−0.26	UV-3	[116]
$Ge(C_6H_5)_2Ge(C_6H_5)_3$	−0.22	UV-2	[116]
$CH_2Ge(CH_3)_3$	−0.65	UV-2	[109*]
$CH_2Ge(CH_3)_3$	−0.64	IP	[114*]
$CH_2Ge(CH_3)_3$	[−0.63±0.02]	UV-2	[67]
$CH_2Ge(CH_3)_3$	−0.61	UV-2	[67,120*]
$CH_2Ge(CH_3)_3$	−0.4	NMR-C-B	[55]
$CH_2GeH_2(C_2H_5)$	−0.64	UV-2	[109*]
$CH_2Ge(C_2H_5)_3$	−0.67	UV-2	[67,120*]
$CH_2Ge(C_2H_5)_3$	−0.67	UV-2	[49]
$CH_2Ge(C_6H_5)_3$	(−0.60)	UV-1	[66]
$CH_2Ge(C_6H_5)_3$	−0.6	UV-1	[126]
$CH_2Ge(C_6H_5)_3$	−0.52	UV-2	[67,120*]
$CH_2Ge(C_6H_5)_3$	[−0.52±0.02]	UV-2	[67]
$CH_2Ge(OC_2H_5)_3$	−0.39	UV-2	[67,120*]
$CH_2GeH_2(CH_2C_6H_5)$	−0.59	UV-2	[109*]
$CH_2GeH(CH_2C_6H_5)_2$	−0,59	UV-2	[67,120*]
$CH_2Ge(CH_2C_6H_5)_3$	−0.57	UV-2	[67,120*]
$CH_2CH_2Ge(OC_2H_5)_3$	−0.16	UV-2	[120*]
$Sn(CH_3)_3$	[−0.34]	UV-2	[116]
$Sn(CH_3)_3$	−0.30	IP	[114*]
$Sn(CH_3)_3$	(−0.12)	X	[122]
$SnH(C_6H_5)_2$	−0.11	IP	[123*]
$Sn(C_6H_5)_3$	−0.07	UV-2	[116,133*]
$Sn(C_6H_5)_2Cl$	+0.04	IP	[116,123*]
$SnCl_3$	+0.41	IP	[134]
$CH_2Sn(CH_3)_3$	(−0.92)	UV-1	[126]
$CH_2Sn(CH_3)_3$	−0.91	UV-1	[66]
$CH_2Sn(CH_3)_3$	−0.9	UV-1	[65]
$CH_2Sn(CH_3)_3$	−0.82	UV-2	[67,135*]
$CH_2Sn(CH_3)_3$	[−0.81±0.02]	UV-2	[67]
$CH_2Sn(CH_3)_3$	−0.78	IP	[114*]
$CH_2Sn(CH_3)_3$	−0.76	X	[65]
$CH_2Sn(CH_3)_3$	−0.45	NMR-C-B	[55]
$CH_2Sn(C_6H_5)_3$	(−0.81)	UV-1	[66]
$CH_2Sn(C_6H_5)_3$	−0.75	UV-1	[126]
$CH_2Sn(C_6H_5)_3$	[−0 73±0.02]	UV-2	[67]
$CH_2Sn(C_6H_5)_3$	−0.69	UV-2	[65*,67]
$OSn(C_6H_5)_3$	−1.55 (CH_2Cl_2)	IR-NB	[61]
$OSn(C_6H_5)_3$	−2.34 (DMSO)	IR-NB	[61]
$SSn(C_6H_5)_3$	−0.08 (CH_2Cl_2)	IR-NB	[61]
$SSn(C_6H_5)_3$	−0.35(DMSO)	IR-NB	[61]
$Pb(C_6H_5)_3$	−0 07	UV-2	[116,133*]
$CH_2Pb(CH_3)_3$	−1,03±0.03	UV-2	[67][a]
$CH_2Pb(CH_3)_3$	−0.52	NMR-C-B	[55]
$CH_2Pb(C_6H_5)_3$	(−1.08)	UV-1	[65]
$CH_2Pb(C_6H_5)_3$	−1.0	UV-1	[126]
$CH_2Pb(C_6H_5)_3$	−1.0	UV-1	[66]
$CH_2Pb(C_6H_5)_3$	−0.92	UV-2	[65*,67]
$CH_2Pb(C_6H_5)_3$	[−0,90±0.02]	UV-2	[67]
$CH_2CH_2Pb(C_6H_5)_3$	(−0.3)	X	[65]
$CH_2CH_2Pb(C_6H_5)_3$	−0,22	UV-1	[65]
$CH_2CH_2Pb(C_6H_5)_3$	[−0.08]	UV-2	[65*,67]
$OPb(C_6H_5)_3$	−1.79 (CH_2Cl_2)	IR-NB	[61]
$OPb(C_6H_5)_3$	−3.13 (DMSO)	IR-NB	[61]
$SPb(C_6H_5)_3$	−0.28 (CH_2Cl_2)	IR-NB	[61]
$SPb(C_6H_5)_3$	−0.52 (DMSO)	IR-NB	[61]

Notation: IR-NB—analysis of the intensities of the stretching vibration bands of the NO_2 group in the IR spectra of *para*-substituted nitrobenzenes;[61] for the significance of the remaining designations of the methods, see the footnotes to Tables 1 and 7.

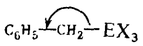
Note: The solvents are indicated in brackets.

[a] Taking into account the data in Refs.65, 113, 131, and 132.

The enhancement of the σ,π conjugation, characterised by the difference $\sigma_p^+ - \sigma_p$ is greater the greater the polarisability of the chemical bonds of the $C_{Ar}EX_3$ fragment of the $C_6H_5EX_3$ fragment of the $C_6H_5EX_3$ molecule and hence the greater the bond refraction ΣR_D, which is a quantitative measure of the polarisability. Therefore linear relations between $\sigma_p^+ - \sigma_p$ and ΣR_D hold for silicon and the germanium compounds and also for any other phenyl derivatives of non-transition Group II–V elements.[116]

The constants σ_p^+ of the groups $E(CH_3)_3$ reflect the influence of oppositely directed effects—the $(p-d)\pi$ interaction and the σ,π conjugation. The former effect is most significant for E = Si or Ge and the corresponding values of σ_p^+ (−0.13 and −0.21) are therefore greater than for $C(CH_3)_3$ (−0.26). On passing to $Sn(CH_3)_3$, the σ,π conjugation intensifies and σ_p^+ diminishes (to −0.34). With enhancement of the electron-accepting properties of X in EX_3, the constants σ_p^+ increase.

On passing from EX_3 to the substituents CH_2EX_3, the constants σ_p^+ diminish sharply, i.e. the negative values of these constants are significantly greater than the corresponding values of σ_p. This is caused by the intensification of the σ,π conjugation



$C_6H_5-CH_2-EX_3$

in the present of a positive charge on the ring. The linear relation between $\sigma_p^+ - \sigma_p$ and $\sum R_D$, which holds for $C_6H_5.CH_2EX_3$, is also valid for alkylbenzenes, although the σ,π conjugation in the latter is comparatively weak.[116] It follows from the analysis of the values of σ_p^+ that the electron-donating properties of the substituents CH_2EX weaken following the enhancement of the electron-accepting properties of X and intensify with increase of the atomic number of E. These features of the σ,π conjugation have been discussed in greater detail in other communications.[44,67,116]

The properties of the σ_p^+ constants of organoelemental substituents reflect the dependence of σ_p^+ on the type of reaction series and on the degree of conjugation between the substituent and the reaction centre, which is familiar[19] for carbon compounds. Comparison of the constants σ_p^+, determined for the same substituent by methods based on the NMR and UV spectroscopy of CTC, indicates a marked discrepancy between the results. According to the UV spectroscopic data for CTC, the substituents $CH_2E(CH_3)_3$ are much stronger electron donors, the discrepancy between the results obtained by the two methods increasing with increase of the atomic number of E. Under the experimental conditions of the UV spectroscopic measurements for CTC, there is an appreciable positive charge on the aromatic ring, which leads to an increase of the degree of σ,π conjugation. The constants σ_p^+ then reach high negative values, which is inconsistent with the data obtained by the NMR method, where there is no positive charge on the ring in the ground electronic state.

Thus in the experiments involving the NMR and UV spectroscopic measurements for CTC, the substituent $CH_2E(CH_3)_3$ is in essence linked to different reaction centres (neutral and positively charged). The constants σ_p^+ therefore do not remain invariant, reflecting the unequal degrees of conjugation of the substituent $CH_2E(CH_3)_3$ with different reaction centres. Analogous situations have been discussed for organic compounds.[112,116]

5. Other σ Constants

Systematic studies of other constants of organoelemental substituents are only just beginning. Only scattered data are available on the constants σ_p^- of the substituents $Si_n.(CH_3)_{2n+1}$ (where $n = 1,2,3$),[59,69,121,136] $Si(C_6H_5)_3$, and $Ge(C_6H_5)_3$;[73] the constants σ_R^- and σ_R^+ of the silantranyl and trialkoxysilyl groups[52] and $COOCH_2SiF_3$,[83] $OE(C_6H_5)_3$, and $SE(C_6H_5)_3$, where E = Sn or Pb,[61] have also been obtained.

The steric effects in organoelemental compounds[45] are distinguished by a number of features. Therefore, together with the accumulation of data on the steric constants E_S of silyl substituents,[137] the constants $E_S(Si)$,[138] reflecting the specific features of the steric effects of the alkyl groups linked to the silicon atom, have also been introduced.

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In conclusion we may note that the correlation equations linking structure and reactivity have been developed for silicon subgroup compounds to a lesser extent than for carbon derivatives, which can be explained not only by the inadequate extent to which the organoelemental compounds have been investigated and the experimental difficulties in the determination of the σ constants of the element-containing substituents but also by the marked, even more pronounced than for carbon compounds, dependence of these constants on the type of reaction centre. Although, on the one hand, this factor does hold back the use of the σ constants as universal characteristics of the donor–acceptor properties of element-containing substituents, on the other hand, the correlation equations constitute an effective means for the investigation of intramolecular interactions between the silicon subgroup element and the variable reaction centre. Analysis of the accumulated information about the σ constants is therefore of independent interest and leads to prospects for further study of urgent theoretical problems in the organoelemental chemistry of non-transition elements.

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The Phosphorus Analogues of Aminocarboxylic Acids

V.P.Kukhar' and V.A.Solodenko

The review is devoted to aminophosphonic, aminophosphinic, and aminophosphonous acids and their derivatives. The interest in these compounds is in many respects because some of them have been detected in Nature and have an appreciable bioactivity. The review deals with the methods of synthesis of aminophosphonic, aminophosphinic, and aminophosphonous acids and with the properties of these compounds, attention being specially concentrated on the phosphorus analogues of natural α-aminocarboxylic acids.

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I. INTRODUCTION

β-Aminoethylphosphonic acid (ciliatine)—the first natural product with a P–C bond—was isolated from natural sources in 1959.[1] Subsequently other natural aminophosphonic, aminophosphinic, and aminophosphonous acids and their derivatives were discovered.[2–10] The appreciable bioactivity of these compounds stimulated interest in the study of their chemistry and bioreactions. The phosphorus analogues of natural aminocarboxylic acids have attracted special attention. These compounds belong to the class of aminoalkyl organophosphorus compounds, whose chemistry has been considered in a number of reviews.[11–13] At the same time, the presence in their structure of the free amino-group, frequently in combination with other functional groups (hydroxy-, mercapto-, etc.), imposes definite limitations on the choice of methods and frequently requires special approaches to their synthesis. Stereochemical aspects are also important.

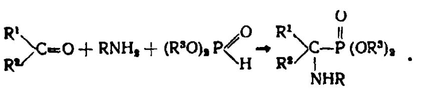
The chemistry of α-aminophosphonic acids has been examined in a review[14] published in 1975, but during the intervening period has been significantly supplemented by new results. A later review[15] on the chemistry of aminophosphinic acids is extremely concise.

This review deals with the methods of synthesis of aminophosphonic, aminophosphinic, and aminophosphonous acids (APA) and their properties. Attention is concentrated on the phosphorus analogues of natural α-aminocarboxylic acids.

II. METHODS OF SYNTHESIS OF AMINOPHOSPHONIC, AMINOPHOSPHINIC, AND AMINOPHOSPHONOUS ACIDS

1. Amino- and Amido-alkylation of Hydrophosphoryl Compounds; the Kabachnik–Fields Reaction

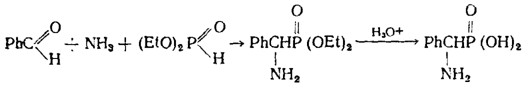
At the beginning of the 1950's, Kabachnik and co-workers[16–21] and independently the American investigator Fields[22] showed that the interaction of ammmonia (or an amine), a carbonyl compound, and a dialkyl phosphite leads to the formation of α-aminophosphonic acid esters (the Kabachnik–Fields reaction):



$$R^1R^2C{=}O + RNH_2 + (R^3O)_2P(O)H \rightarrow R^1R^2C(NHR){-}P(O)(OR^3)_2 \,.$$

It has been suggested that the reaction mechanism involves the initial formation of an α-hydroxyalkylphosphonic acid ester with the subsequent replacement of the hydroxy-group by the amino-group.[23] Another view on the mechanism of this reaction has been described in a monograph,[24] where the reaction is treated as aminoalkylation of a hydrophosphoryl compound (HPC) by an electrophilic intermediate formed form the carbonyl compound and the amine.

The range of compounds which can be involved in this process is extremely large.[23,24] We shall deal only with studies where the synthesis of α-APA† with an unsubstituted amino-group has been described. The most convenient method for the synthesis of these compounds uses ammonia as the amino-component.[16–21,25] When benzaldehyde, an alcoholic ammonia solution, and diethyl phosphite are heated in a sealed tube at 100 °C, diethyl α-aminobenzylphosphonate is formed, its hydrolysis leading to free α-aminobenzylphosphonic acid:[16,18]



$$PhC(O)H + NH_3 + (EtO)_2P(O)H \rightarrow PhCH(NH_2)P(O)(OEt)_2 \xrightarrow{H_3O^+} PhCH(NH_2)P(O)(OH)_2 \,.$$

Phosphonic analogues of alanine (Ala^P) and phenylalanine (Phe^P) have been obtained by this method.[26] The yields of α-aminophosphonic acid esters synthesised in this way do not usually exceed 45%. Diethyl α-aminoethylphosphonate has been obtained in 76% yield by a somewhat modified method (stirring of a mixture of acetaldehyde–ammonia, diethyl phosphite, and ammonia in a sealed tube at room temperature).[27] The use of acid esters of phosphonous acids makes it possible to obtain derivatives of α-aminophosphinic acid.[20] The phosphonic and phosphinic analogues of cycloleucine were obtained in this way, starting from the diethylketal of cyclopentanone

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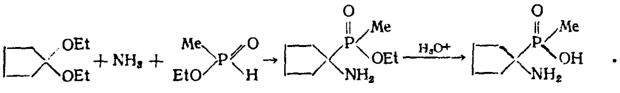
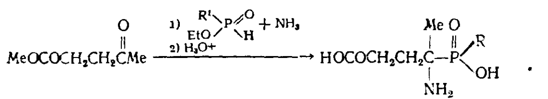
†The APA which are analogues of natural aminocarboxylic acids are designated by the generally accepted three letter abbreviations with the superscript P. For the phosphorus analogues of aspartic and glutamic acids, the additional subscripts α, β, and γ, denoting the position of the phosphorus-containing group, are introduced. For the phosphine analogues, a superscript indicating the position of the substituent at the phosphorus atom is added.

and diethyl phosphite or ethyl methylphosphonite respectively:[28]



The α-phosphonic and α-phosphinic analogues of α-methylglutamic acid has been synthesised analogously by the aminoalkylation of diethyl phosphite and ethyl methylphosphonite:[29]

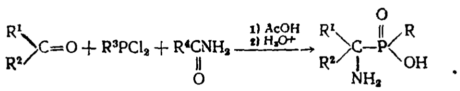


R = OH, Me

Overall, the Kabachnik–Fields reaction is a convenient general method for synthesis of α-aminophosphonic and α-aminophosphinic acids; the important advantages of the method are a single-stage process and the availability of the starting compounds.

The aminoalkylation of HPC has been extended to tervalent phosphorus acids—hypophosphorus, phosphorous, and phosphonous acids, which made it possible to obtain directly free α-aminophosphonous,[30,31] α-aminophosphonic,[32] and α-aminophosphinic,[33,34] acids. However, this approach has not found extensive application in the synthesis of α-APA with a free amino-group because it is restricted almost exclusively to the aminoethylation reaction. The report[35] of the synthesis of a series of α-(*N*-benzylamino)alkylphosphonic acids by the aminoalkylation of phosphorous acid was subsequently judged to be erroneous.[36] It is noteworthy that the aminoalkylation of phosphorous acid is used extremely widely for the synthesis of APA derivatives with valuable complex-forming properties.[12,13]

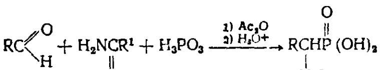
The reaction involving the amidoalkylation of tervalent phosphorus halides has found very extensive application in the synthesis of α-APA. When a carbonyl compound, phosphorus trichloride [or an alkyl(aryl)dichlorophosphine], and a compound containing the amide group interact in acetic acid, an intermediate is formed, whose hydrolysis leads to the formation of α-aminophosphonic or α-aminophosphinic acid in 40–60% yield:[37]



R^3 = Cl, Alk, Ar; R^4 = EtO, $PhCH_2O$;
R = OH, Alk, Ar

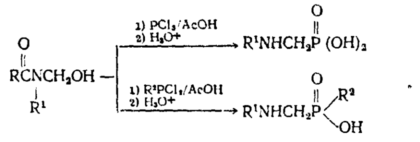
The use of acetals instead of carbonyl compounds and of carboxylic acid amides (acetamide, benzamide) instead of carbamates lowers the yield of α-APA. It is of course not permissible to employ amines and ammonia in this reaction.[37] The process can be carried out successfully also in trimethylacetic acid.[38] Aminomethylphosphonic acid (Gly^P) [39] as well as the phosphonic and phosphinic analogues of cycloleucine,[28] proline,[40] serine,[41] α-methylaspartic, α-methylpyroglutamic, glutamic, and pyroglutamic acids,[42] and ornithine[43] have been obtained by this method. The use of *N*-alkylbenzylcarbamates as the amide components makes it possible to synthesise α-(*N*-alkylamino)alkylphosphonic and the corresponding phosphinic acids.[44] The attempts to employ *NN'*-dialkylbenzylcarbamates in the reaction were unsuccessful.[44]

The amidoalkylation of phosphorous acid in acetic anhydride has been used to obtain phosphonic analogues of alanine, valine, and also other α-aminophosphonic acids (yields from 10 to 75%):[45]



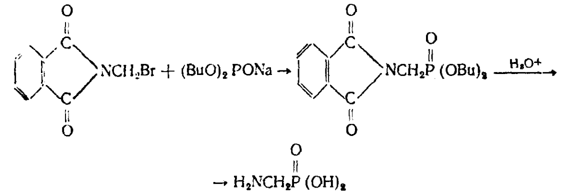
R = Me, iso-Pr, Ar; R^1 = $PhCH_2O$, Ph, Me

The interaction of *N*-hydroxymethylamides with phosphorus trichloride or alkyl(aryl)dichlorophosphines in acetic acid leads to the formation of aminomethylphosphonic or aminomethylphosphinic acid, including *N*-alkylated derivatives, in 25–80% yield:[46–48]



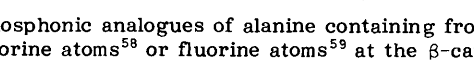
2. The Arbuzov and Michaelis–Becker Reaction

The Arbuzov and Michaelis–Becker reactions have been of fundamental importance for the chemistry of organophosphorus compounds and historically were the first methods of synthesis of aminomethylphosphonic acid—the phosphonic analogue of glycine (Gly^P):[26,49]

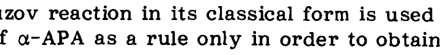


The use of dialkyl phosphonites makes it possible to obtain aminophosphinic acids.[50] The use of the Arbuzov and Michaelis–Becker reactions for the synthesis of β-, γ-, and ω-APA has been described.[49,51–55]

For example, the Arbuzov reaction has been the key stage in the first synthesis of phosphinothricin—a phosphinic analogue of glutamic acid (Glu$^{\gamma\text{-}PMe}$):[9]



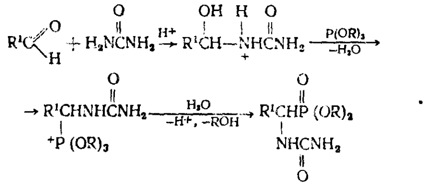
Diethyl α-ethoxycarbonylaminomethylphosphonate—an important intermediate in the synthesis of cephalosporin—has been obtained by the reaction of the ethyl ester α-bromo-*N*-t-butoxycarbonylglycine with triethyl phosphite:[56,57]



$$\underset{\displaystyle Br}{\text{t-BuOCONHCHCOOEt}} \xrightarrow[2)\ HCl/EtOH]{1)\ P(OEt)_3} \underset{\displaystyle COOEt}{H_2NCH\overset{O}{\overset{\|}{P}}(OEt)_2}$$

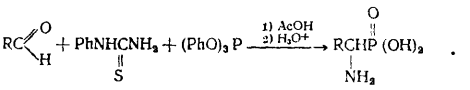
The phosphonic analogues of alanine containing from one to three chlorine atoms[58] or fluorine atoms[59] at the β-carbon atom have been obtained by the Arbuzov reaction.[59] The long duration and relatively severe reaction conditions can be regarded as disadvantages of the Arbuzov reaction as a method of synthesis of APA. In certain cases this method does not yield satisfactory results. Thus the phosphinic analogue of alanine (Ala^{P-Ph}) has been obtained by the Arbuzov reaction in only 5% yield.[50]

The Arbuzov reaction in its classical form is used for the synthesis of α-APA as a rule only in order to obtain aminomethylphosphonic and aminomethylphosphinic acids and their derivatives. On the other hand, the non-classical variants of the Arbuzov reaction, where electrophiles other than alkyl halides are introduced into the reaction with tervalent phosphorus acid esters, have found extremely extensive applications in the synthesis of phosphonic and phosphinic analogues of α-aminocarboxylic acids. Thus it has been found that, on heating with aldehydes and ureas, phosphites and phosphonites give rise to esters of α-ureidophosphonic and the corresponding phosphinic acids. Mono- and di-substituted ureas produce only monophosphonates, while unsubstituted urea gives rise to a mixture of mono- and di-phosphonates. Instead of urea, thiourea may be employed. The reaction is facilitated in the presence of acid catalysts. The following process mechanism has been discussed:[60]



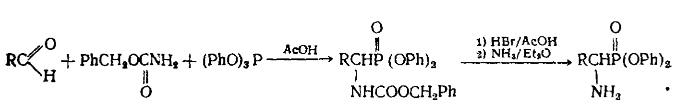
$$\mathrm{R^1CHO} + \mathrm{H_2NC(O)NH_2} \xrightarrow{H^+} \mathrm{R^1CH(OH)-\overset{+}{N}H-C(O)NH_2} \xrightarrow[-H_2O]{P(OR)_3} \mathrm{R^1CH(\overset{+}{P}(OR)_3)NHC(O)NH_2} \xrightarrow[-H^+,\,-ROH]{H_2O} \mathrm{R^1CH(NHC(O)NH_2)P(O)(OR)_2}\ .$$

This process is the basis of a series of methods of synthesis of α-APA and their derivatives. Thus, when an aldehyde, *N*-phenylthiourea, and triphenyl phosphite are heated in acetic acid, the diphenyl esters of α-thioureidoalkylphosphonic acid esters are formed and their hydrolysis leads to the free α-aminoalkylphosphonic acids:



$$\mathrm{RCHO} + \mathrm{PhNHC(S)NH_2} + \mathrm{(PhO)_3P} \xrightarrow[2)\ H_3O^+]{1)\ AcOH} \mathrm{RCH(NH_2)P(O)(OH)_2}\ .$$

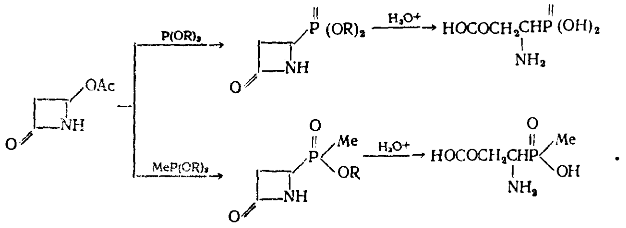
A series of α-APA, including the phosphonic analogues of alanine, valine, phenylalanine,[61] methionine,[62,63] cysteine, and cystine,[64] have been obtained by this method. Instead of *N*-phenylthiourea, unsubstituted thiourea,[61] *N*-(α-phenylethyl)thiourea,[61] and ethyl- or benzyl-carbamates[65] can be used in the reaction. The *N*-benzyloxycarbonyl derivatives of α-APA formed when benzylcarbamate is used are smoothly converted into the diphenyl esters of α-aminophosphonic acids on treatment with hydrogen bromide in glacial acetic acid, which constitutes a convenient method of synthesis of these compounds:[66]



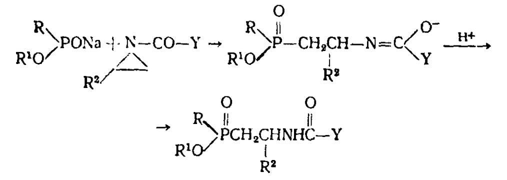
$$\mathrm{RCHO} + \mathrm{PhCH_2OC(O)NH_2} + \mathrm{(PhO)_3P} \xrightarrow{AcOH} \mathrm{RCH(NHCOOCH_2Ph)P(O)(OPh)_2} \xrightarrow[2)\ NH_3/Et_2O]{1)\ HBr/AcOH} \mathrm{RCH(NH_2)P(O)(OPh)_2}\ .$$

The phosphonic analogues of valine and phenylglycine have been obtained by the hydrolysis of α-ureidoalkylphosphonates, formed on heating a mixture of *N*-phenylurea, triethyl phosphite, and the corresponding aldehyde in toluene in the presence of boron trifluoride etherate.[67] When an *N*-monosubstituted urea, obtained from the optically active α-phenylethylamine, is used in this reaction, asymmetric induction is observed and the optically active α-aminophosphonic acid is formed (but the enantiomeric excess is small).[68]

4-Acetoxyazetidin-2-ones readily react with phosphites and phosphonites to form 2-oxoazetidin-4-ylphosphonates and the corresponding phosphinates; the acid hydrolysis of the resulting compounds affords the phosphonic and phosphinic analogues of aspartic acid ($Asp^{\alpha-P}$ and $Asp^{\alpha-P-Me}$):[69-71]



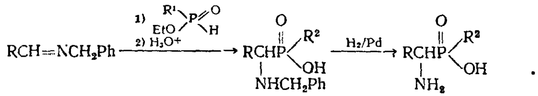
The esters of tervalent phosphorus acids enter into the Arbuzov and Michaelis–Becker reactions with *N*-acyl- or *N*-sulphonyl-aziridines to form derivatives of α-aminoethylphosphonic and the corresponding phosphinic acid:[72-74]



On interaction with phosphites, *N*-(trimethylammoniamethyl)-formamide gives rise to esters of *N*-formylaminomethylphosphonic acid.[75] The reaction of diethyl methylphosphonite proceeds analogously.[15]

3. The Addition of Hydrophosphoryl Compounds to Carbon–Nitrogen and Carbon–Carbon Multiple Bonds

The addition of HPC to the carbon–nitrogen double bond is an important general method for the formation of the P–C–N bond system.[11,13,24] The addition of HPC to Schiff bases, choosing a substituent at the nitrogen atom which can be removed with formation of a free amino-group, is most often employed for the synthesis of α-APA. Many α-aminophosphonic and α-aminophosphinic acids, for example, have been obtained by the addition of acid phosphites and phosphonites to aldimines based on benzylamine, since the *N*-benzyl group is readily removed by hydrogenolysis in the presence of the palladium catalyst:[76,77]



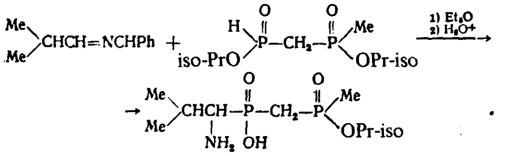
$$\mathrm{RCH{=}NCH_2Ph} \xrightarrow[2)\ H_3O^+]{1)\ R^1(EtO)P(O)H} \mathrm{RCH(NHCH_2Ph)P(O)(R^2)(OH)} \xrightarrow{H_2/Pd} \mathrm{RCH(NH_2)P(O)(R^2)(OH)}\ .$$

R^1 = OAlk, Alk, Ar; R^2 = OH, Alk, Ar

The *N*-α-phenylethyl group is also removed by catalytic hydrogenolysis.[78-80] The addition of dialkyl phosphites to aldimines, obtained from the optically active α-phenylethylamine, is accompanied by appreciable asymmetric induction, which has been used for the asymmetric synthesis of α-aminophosphonic acids.[78,79,81] The highest degree of asymmetric induction (up to 80% optical purity) has been observed in acid catalysis (HCl, AcOH); with increase of temperature, the stereoselectivity of the addition diminishes appreciably. Diethyl phosphite can be replaced in this reaction successfully by tris(trimethylsilyl) phosphite.[80]

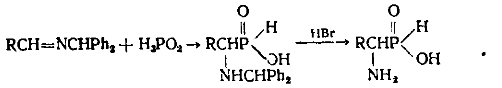
Together with dialkyl phosphites, mono-, bis-,[82] and tris-(trimethylsilyl) phosphites[80] also add to Schiff bases. The silyl esters of α-aminophosphonic acids formed are readily hydrolysed under neutral conditions (on heating with water or alcohol) to the free acids, which facilitates the isolation of the latter.

The addition of acid esters of methylenediphosphonic acids to Schiff bases has been described:[83]



$$\mathrm{Me_2CHCH{=}NCHPh + H(iso\text{-}PrO)P(O){-}CH_2{-}P(O)(Me)(OPr\text{-}iso) \xrightarrow{1)\,Et_2O;\ 2)\,H_3O^+} Me_2CH\underset{NH_2}{CH}{-}\underset{OH}{P}(O){-}CH_2{-}P(O)(Me)(OPr\text{-}iso)}$$

Phosphorous acid usually reduces Schiff bases to secondary amines and products of addition to the C=N bonds can be obtained in satisfactory yields only in isolated instances.[84] In contrast to phosphorous acid, hypophosphorous acid adds fairly smoothly to Schiff bases with formation of *N*-substituted α-aminophosphonous acids.[85] Many α-aminophosphonous acids, including the phosphonous analogues of all the most important natural α-aminocarboxylic acids, have been obtained in this way:[86–89]



$$\mathrm{RCH{=}NCHPh_2 + H_3PO_2 \rightarrow \underset{NHCHPh_2}{RCH}P(O)(H)(OH) \xrightarrow{HBr} \underset{NH_2}{RCH}P(O)(H)(OH)}$$

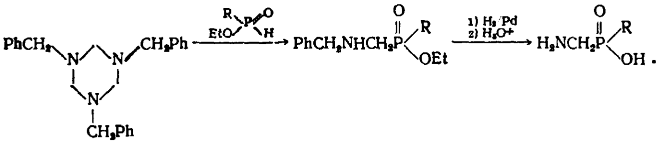
Catalytic hydrogenolysis is unsuitable in this instance for the removal of the protecting group owing to the poisoning of the catalyst by the hydrophosphoryl compound and for this reason azomethines with the *N*-diphenylmethyl substituent, which is readily removed in an acid medium, are employed.

The addition of dialkyl phosphites to azomethines with the acid-removable *N*-diphenylmethyl substituent has been used to synthesise phosphonic analogues of alanine, valine, phenylalanine, and cycloleucine;[90] mono- and di-aminodiphosphonic acids, including the diphosphonic analogues of aspartic and glutamic acids, have been synthesised in this manner.[91]

The application of other *N*-protecting groups, removable by acid hydrolysis, for the synthesis of α-APA has been described, namely the t-butyl,[92] 1-phenylcyclopentyl,[93,94] and αα-disubstituted benzyl[95] groups.

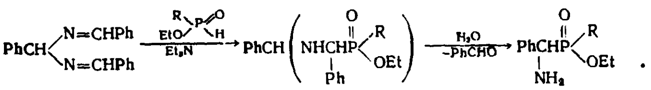
The addition of HPC to azomethines has been used widely in the synthesis of various α-APA, in particular potential bacteriostatic compounds,[96] analogues of morphactins (plant growth regulators),[97–100] phosphorus analogues of penicillamine,[101] and spin-labelled compounds.[102]

Hexahydrotriazines react with acid phosphites and phosphonites to form esters of *N*-substituted α-aminophosphonic and the corresponding phosphinic acids:[15,33,92,103]



Phosphinic analogues of glycine ($\mathrm{Gly^{P-R}}$) (R = Me or Et)[15] as well as the phosphonic analogue of proline[104] have been obtained by this method. The latter compound has also been synthesised by the addition of diphenyl phosphite to monomeric 1-pyrroline.[77] Aminomethylphosphonous acid ($\mathrm{Gly^{P-H}}$) has been synthesised by adding hypophosphorous acid to 1,3,5-tris(diphenylmethyl)hexahydrotriazine in 10% yield.[88]

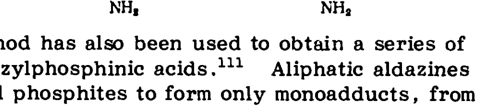
Hydrobenzamide combines with two equivalents of dialkyl phosphite or a monoester of phenylphosphonous acid to form phosphorus-containing aminals, the controlled hydrolysis of which affords the esters of α-aminobenzylphosphonic and the corresponding phosphinic acids:[105,106]



$$\mathrm{PhCH(N{=}CHPh)_2 \xrightarrow[Et_3N]{R(EtO)P(O)H} PhCH\left(NH\underset{Ph}{CH}P(O)(R)(OEt)\right)_2 \xrightarrow[-PhCHO]{H_2O} Ph\underset{NH_2}{CH}P(O)(R)(OEt)}$$

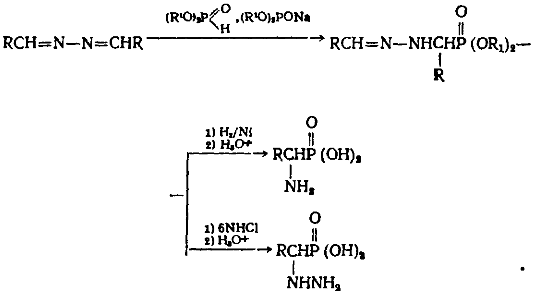
NN'-Dialkylidene-1,2-diaminoalkanes, formed from ammonia and aliphatic aldehydes, behave similarly, which has been used to obtain the esters of certain α-aminophosphonic acids, including the dialkyl esters of the phosphonic analogues of valine.[107]

α-Aminophosphonic acid can be obtained also from aldazines by adding HPC to the C=N bond with subsequent reductive cleavage of the nitrogen–nitrogen bond. Aromatic aldazines combine with two equivalents of dialkyl phosphite and the resulting adducts are reduced with an excess of sodium dialkyl phosphite to esters of α-aminobenzylphosphonic acids:[108–110]



$$\mathrm{XC_6H_4{-}CH{=}N{-}N{=}CH{-}C_6H_4X \xrightarrow{(RO)_2P(O)H,\ (RO)_2PONa} XC_6H_4{-}\underset{NH_2}{CH}P(O)(OR)_2 \xrightarrow{H_3O^+} XC_6H_4{-}\underset{NH_2}{CH}P(O)(OH)_2}$$

This method has also been used to obtain a series of α-aminobenzylphosphinic acids.[111] Aliphatic aldazines react with dialkyl phosphites to form only monoadducts, from which α-hydrazinophosphonic acids can be obtained by acid hydrolysis[112] or α-aminophosphonic acids can be produced by hydrogenation on Raney nickel:[112,113]



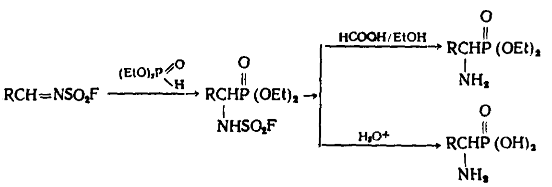
$$\mathrm{RCH{=}N{-}N{=}CHR \xrightarrow{(R'O)_2P(O)H,\ (R'O)_2PONa} RCH{=}N{-}NH\underset{R}{CH}P(O)(OR_1)_2}$$

$$\mathrm{\xrightarrow{1)\,H_2/Ni;\ 2)\,H_3O^+} \underset{NH_2}{RCH}P(O)(OH)_2 \qquad \xrightarrow{1)\,6N\,HCl;\ 2)\,H_3O^+} \underset{NHNH_2}{RCH}P(O)(OH)_2}$$

Acid phosphonites interact similarly with aliphatic aldazines, which makes it possible to obtain α-aminophosphinic acids.[114] This method has been used to obtain phosphonic and phosphinic analogues of alanine, valine, and leucine. The phosphonic and phosphinic analogues of cycloleucine have been synthesised analogously by adding one mole of diethyl phosphite or ethyl methylphosphonite respectively to the ketazine based on cyclopentanone.[28]

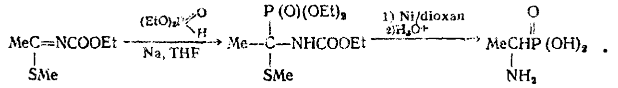
HPC can also be added to a series of other compounds with a C=N bond, which has been employed to synthesise α-APA. For example, benziminoethyl ether combines with two equivalents of dialkyl phosphite to form the ester of the N-phosphorylated α-aminobenzylphosphonic acid.[115] It has been suggested that iminoesters are intermediates in the reaction of orthoformate, a primary amine, and a dialkyl phosphite (or a monoalkyl phosphonite), which results in the formation of aminomethylenebis(phosphonates) or aminomethylenebis(phosphinates).[15,116]

Dialkyl phosphites add to *N*-acylimines to form the esters of *N*-acylated α-aminophosphonic acids.[117,118] Hydrolysis of these compounds leads to α-aminophosphonic acids; it is sometimes possible to remove selectively the *N*-acyl group with formation of esters of α-aminophosphonic acid:[119]



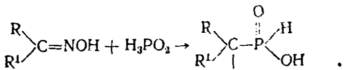
$$\mathrm{RCH{=}NSO_2F \xrightarrow{(EtO)_2P(O)H} \underset{NHSO_2F}{RCH}P(O)(OEt)_2 \rightarrow \left\{ \xrightarrow{HCOOH/EtOH} \underset{NH_2}{RCH}P(O)(OEt)_2 ;\ \xrightarrow{H_3O^+} \underset{NH_2}{RCH}P(O)(OH)_2 \right.}$$

N-Acyliminothioesters are capable of reacting with dialkyl phosphites analogously to *N*-acylimines. The reductive elimination of alkylthio-groups from the adducts and subsequent hydrolysis lead to α-aminophosphonic acids:[126]



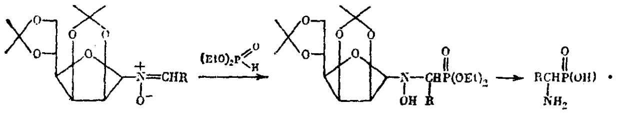
This method has been used to synthesise the enantiomers of the phosphonic analogue of phenylalanine.[121]

Under the conditions of alkaline catalysis, oximes combine with two equivalents of dialkyl phosphite to form *N*-phosphorylated α-aminophosphonates as a result of the postulated aminophosphonate–amidophosphate [phosphoramidate?] rearrangement.[122] The addition of hypophosphorous acid to oximes, which leads to the formation of α-aminophosphonous acids, is of considerable interest. The phosphonous analogues of alanine, valine, and glutamic acid ($\mathrm{Glu}^{\alpha-\mathrm{P-H}}$) have been obtained by this method:[123]



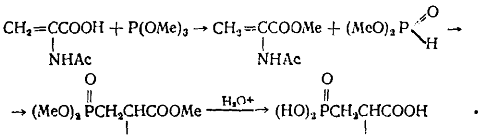
The mechanism of this reaction has not been elucidated.

The addition of dialkyl phosphites to *N*-glycosylnitrones has been used for the asymmetric synthesis of dextrorotatory phosphonic analogues of serine, valine, and alanine:[124]

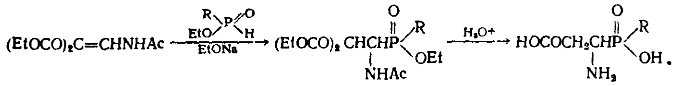


Dialkyl phosphites[125] and phosphorous acid[126,127] add to nitriles with formation of aminomethylenediphosphonic acids or their esters. Under the conditions of base catalysis, dialkyl phosphites react with arylisonitriles to form *N*-arylaminomethylenediphosphonates.[128]

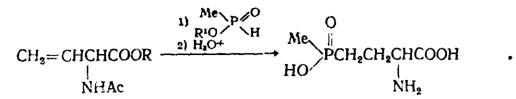
The ability of HPC to undergo Michael addition to activated carbon–carbon double bonds has also been used to synthesise α-, β-, and γ-APA. The phosphonic analogue of aspartic acid $\mathrm{Asp}^{\beta-\mathrm{P}}$, where the β-carboxy-group has been replaced by the phosphono-group, has been obtained by the interaction of α-acetamidoacrylic acid with phosphite:[129]



The addition of esters of methyl- and ethyl-phosphonous acids to α-acetamidoacrylic acid proceeds with formation of the corresponding phosphonic analogue of aspartic acid ($\mathrm{Asp}^{\beta-\mathrm{P-Me}}$ and $\mathrm{Asp}^{\beta-\mathrm{P-Et}}$).[130] The phosphonic and phosphinic analogues of aspartic acids, in which the phosphono- or phosphino-group replaces the α-carboxy-group, have been obtained by the addition of dialkyl phosphites or acid phosphonites to acetamidomethylenemalonate with subsequent hydrolysis and decarboxylation of the adducts:[130,131]

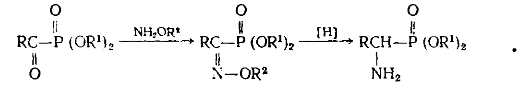


The esterification of the carboxy-groups in these compounds with subsequent ammonolysis leads to the formation of the phosphonic and phosphinic analogues of asparagine.[130,131] The phosphonic and phosphinic analogues of α-methylaspartic acid have been obtained by adding the corresponding HPC to β-aminocrotonate.[29] The same approach has been used to obtain the phosphinic analogue of glutamic acid—phosphinothricin ($\mathrm{Glu}^{\gamma-\mathrm{P-Me}}$):[15]



4. Amination of α-Oxophosphonates (The Oxime Method)

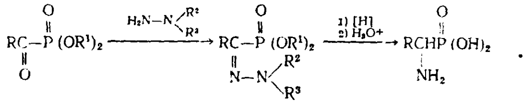
A number of methods of synthesis of α-aminophosphonic and α-aminophosphinic acids are based on the use of α-oxoalkylphosphonates and the corresponding phosphinates, which are converted into oximes and then reduced (the oxime method):



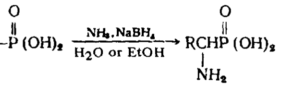
The oxime group can be reduced by a wide variety of reductants. Thus α-aminobenzylphosphonic acid and its derivatives[132] and also the phosphonic analogue of dihydroxyphenylalanine (DOPA) [133] have been obtained by the reduction of the corresponding oximes with aluminium amalgam. Diborane has also been used as the reductant;[134] the phosphonic analogues of alanine, valine, leucine, and isoleucine have been obtained in this way. The oximes can be reduced by hydrogenation on Raney nickel,[135,136] which has been used in the synthesis of the phosphonic analogues of tryptophan.[136]

In the reduction of oximes with zinc in formic acid, the amino-group formed is partly formylated; to achieve deformylation, the reaction mixture is treated with hydrogen chloride in methanol.[137] The esters of phosphonic analogues of alanine, valine, leucine, phenylalanine, glutamic acid, and methionine,[137] as well as the phosphonic analogue of cysteine[138] have been synthesised by this procedure. The reduction of oximes with zinc in formic acid has also been employed for the synthesis of α-aminophosphonic acids.[42]

α-Oxophosphonates can be converted into hydrazones, whose reduction with aluminium amalgam[139] or zinc in a mixture of acetic and trifluoroacetic acids[140] as well as catalytic hydrogenation[139,140] lead to α-aminophosphonates:



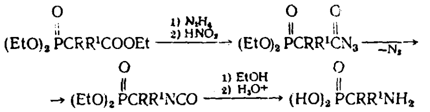
The single-stage method for the direct conversion of α-oxophosphonic acids into α-aminophosphonic acids on treatment with ammonia and sodium tetrahydroborate[141] is undoubtedly attractive:



The phosphonic analogues of alanine, valine, leucine, phenylalanine, and glutamic acid ($\mathrm{Glu}^{\alpha-\mathrm{P}}$) have been obtained in this way. Instead of ammonia, primary amines can be used in the reaction. It is of interest that the mono- and di-esters of α-oxophosphonic acids do not enter into this reaction. The use of $\mathrm{NaB}^3\mathrm{H}_4$ makes it possible to obtain tritium-labelled α-aminophosphonic acids.[142]

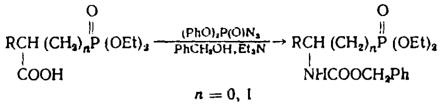
5. Synthesis of Aminophosphonic Acids using the Curtius and Hofmann Rearrangements

One of the most frequently employed methods of synthesis of α-APA is that from the esters of α-phosphonocarboxylic acids, whose key stage is the Curtius rearrangement of the corresponding phosphonocarboxylic acid azides. The general scheme of this multistage synthesis, which is usually carried out as a "single flask" process, i.e. without the isolation of intermediates, is presented below:[129,143]



The phosphonic analogues of glycine, alanine, phenylalanine, valine, α-methylalanine, tyrosine, lysine, ornithine, etc. have been obtained by this procedure.[129,143–145] The method has also been used to synthesise α-aminoethylphosphonic acid (ciliatine) and γ-aminopropylphosphonic acid (the phosphine analogue of γ-aminobutyric acid [146]). The broad limits of its applicability, in particular the possibility of synthesising α-, β-, γ-, and ω-APA as well as αω-diaminophosphonic acids must be regarded as advantages of the methods. Its disadvantage is its multistage nature, which is frequently the reason for the moderate overall yields of the aminophosphonic acids.

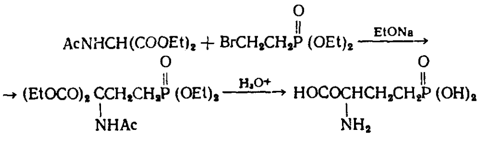
If the rearrangement of the phosphonocarboxylic acid azides is carried out in the presence of alcohols, it is possible to isolate the corresponding carbamates derived from the aminophosphonic acids, which has been used to synthesise N-benzyloxycarbonyl derivatives of α- and β-aminophosphonates:[147]



The Hofmann degradation of phosphonocarboxylic acid amides can also be used to synthesise aminophosphonic acids. This method has been used successfully to obtain β-aminoethylphosphonic acid[148] and its derivatives.[149,150] On the other hand, there are contradictory literature data concerning the possibility of using the Hofmann degradation for the synthesis of α-aminophosphonic acids. The successful preparation by this method of a series of α-aminophosphonic acids, including the phosphonic analogues of α-alanine, has been reported.[151] However, it has been shown that, depending on the structure, the phosphonoacetamides $(EtO_2)P(O)CHRC(O).NH_2$ either undergo the Hofmann rearrangement with formation of α-APA (for R = Et or Ph) or are brominated at the α-carbon atom (for R = Me or $PhCH_2$). The phosphonic analogue of α-alanine could not be obtained by this method.[152]

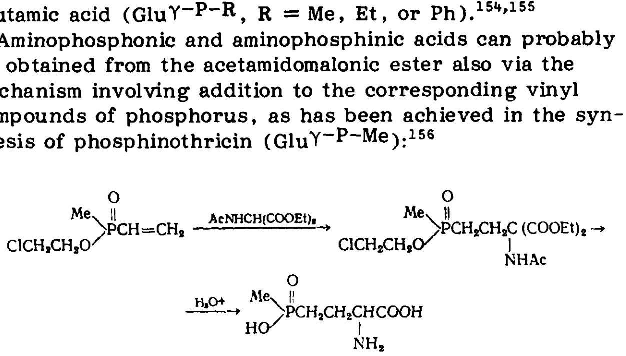
6. Syntheses Using Acetamidomalonic Ester and Vinylphosphonates or Vinylphosphinates

In one of the first specific syntheses of phosphonic analogues of natural aminoacids, the alkylation of acetamidomalonic ester with β-bromoethylphosphonate was used to obtain the analogue of glutamic acid ($Glu^{\gamma-P}$):[153]

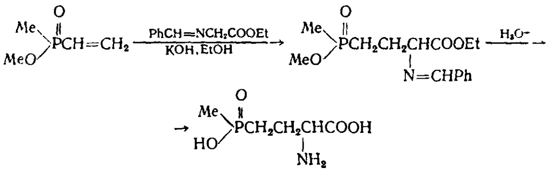


The introduction of β-bromoethylphosphonates into this reaction entailed the formation of phosphinic analogues of glutamic acid ($Glu^{\gamma-P-R}$, R = Me, Et, or Ph).[154,155]

Aminophosphonic and aminophosphinic acids can probably be obtained from the acetamidomalonic ester also via the mechanism involving addition to the corresponding vinyl compounds of phosphorus, as has been achieved in the synthesis of phosphinothricin ($Glu^{\gamma-P-Me}$):[156]

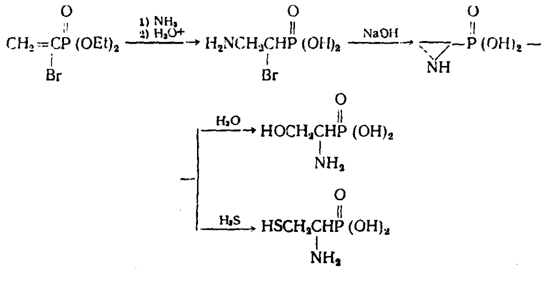


The same method has been used to obtain phosphinic analogues of glutamic acids containing various substituents at the phosphorus atom, including functional groups [$Glu^{\gamma-P-R}$, where R = CH_2COOMe, CH_2COOH, $CH_2CH_2CH(NH_2)COOH$, $CH_2C_6H_4Br$-p, or $PhCH_2$].[115] Certain Schiff bases also undergo Michael addition to methylvinylphosphinate, which has been used successfully to synthesise phosphinothricin:[157]



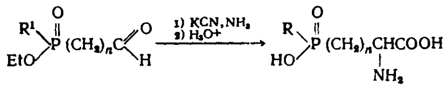
The addition of chiral Schiff bases to vinylphosphonates and vinylphosphinates has been used for the asymmetric synthesis of α-amino-γ-phosphonobutyric acid [(+)-$Glu^{\gamma-P}$] and (+)-phosphinothricin [(+)-$Glu^{\gamma-P-Me}$], as well as their (−)-enantiomers.[158]

Ammonia adds to α-bromovinylphosphonate with formation of β-amino-α-bromoethylphosphonic acid, which cyclises in an alkaline medium to aziridinylphosphonic acid. The opening of the aziridine ring in this acid by treatment with water or hydrogen sulphide leads to the formation of the phosphonic analogues of serine[159,160] and cysteine[138] respectively:



7. Other Methods of Synthesis of Aminophosphonic, Aminophosphinic, and Aminophosphonous Acids

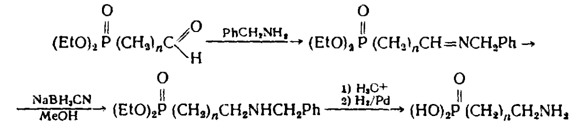
The traditional methodology for the synthesis of aminocarboxylic acids has also been applied to the synthesis of APA. For example, the phosphonic and phosphinic analogues of aspartic and glutamic acids ($Asp^{\beta-P}$ and $Glu^{\gamma-P}$) have been synthesised from β- and γ-oxophosphonates and the corresponding phosphinates using the Strecker reaction:[161,162]



R = OH, Me, Et; n = 1, 2

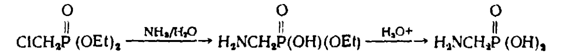
The phosphonic and phosphinic analogues of α-methylaspartic and α-methylglutamic acids can be obtained in the same way.[29] The use of (−)-α-phenylethylamine in the Strecker synthesis makes it possible to obtain phosphonic analogues of aspartic and glutamic acids enriched in the (+)-enantiomers.[163]

β- and γ-Aminophosphonic acids have been synthesised by condensing benzylamines with β- and γ-oxophosphonates with subsequent reduction of the resulting azomethines with sodium cyanohydroborate and the removal of the P-ester and N-benzyl groups by acid hydrolysis and hydrogenation over a palladium catalyst respectively:[164]

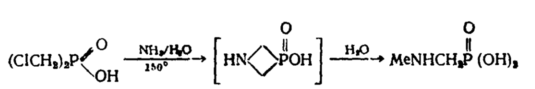


n=1,2

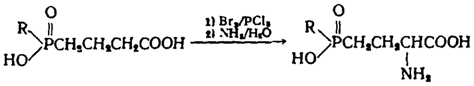
α-Aminophosphonic acids can also be synthesised by the direct substitution of the halogen atoms in α-halogenoalkylphosphonic acids or their derivatives by the amino-group. However, this method is not used frequently, possibly because the substitution by the amino-group in chloromethylphosphonate on treatment with ammonia proceeds under extremely severe conditions and aminomethylphosphonic acid is formed in a moderate yield (20–48%):[165,166]



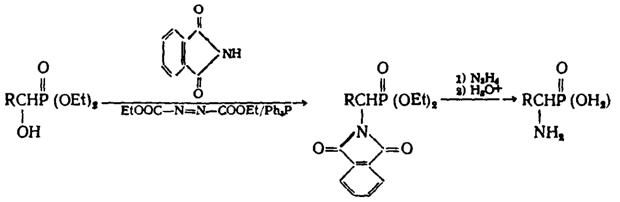
Aminomethylphosphonous acid has been obtained analogously by the reaction of chloromethylphosphonous acid with ammonia.[167] The interaction of ammonia and amines with di(chloromethyl)phosphinic acid has been investigated in a number of studies.[168–171] The products of the reaction of this acid with aqueous ammonia proved to be N-methylaminomethylphosphonic acid, which has been explained by the initial formation of the azaphosphetidine oxide ring, which is cleaved by water at the P–C bond:[168]



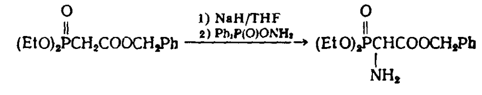
On reaction with di(chloromethyl)phosphinic acid, benzylamine gives rise to di(benzylaminomethyl)phosphinic acid, the catalytic hydrogenolysis of which affords di(aminomethyl)phosphinic acid.[168] The substitution of a halogen atom by the amino-group has been used in the synthesis of phosphonic and phosphinic analogues of glutamic acid (Glu$^{\gamma-P}$ and Glu$^{\gamma-P-Me}$):[172]



α-Aminoalkylphosphonic acids can be obtained from the readily available α-hydroxyphosphonic acids, which are formed from carbonyl compounds and HPC. The substitution of the hydroxy-group by the amino-group is achieved by means of the Mitsunobu reaction between the α-hydroxyphosphonate and phthalimide in the presence of triphenylphosphine and diethyl azodicarboxylate and subsequent removal of the phthalimide group by the standard treatment with hydrazine:[173]

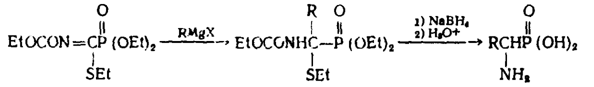


The amino-group can be introduced directly into the α-position in the molecules of phosphonoacetates, which produce stabilised carbanions, by treatment with reagents such as O-(mesitylenesulphonyl)hydroxylamine [174] and O-(diphenylphosphinoyl)hydroxylamine.[175] The α-aminophosphonoacetates formed are important intermediates in the synthesis of cephalosporins:

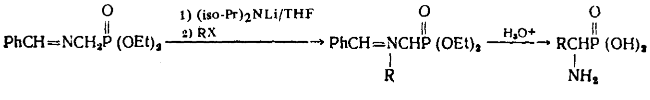


Treatment with trifluoromethanesulphonyl azide results in the introduction in the α-position of phosphonoacetates of the azido-group, whose reduction by catalytic hydrogenation affords α-aminophosphonoacetates.[176]

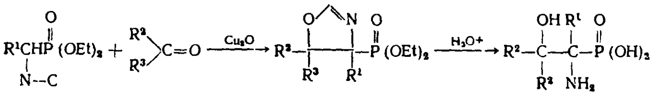
Approaches based on the modification of the P–C–N bond system already formed can also be used in the synthesis of α-aminophosphonic acids. Thus the reaction of a Grignard reagent with α-(N-ethoxycarbonylimino)-α-(ethylthio)methylphosphonate leads to the formation of an adduct, which is converted into an α-aminoalkylphosphonic acid after the reductive elimination of the ethylthio-group and hydrolysis.[177] The phosphonic analogues of alanine, valine, and phenylalanine have been synthesised in this way:



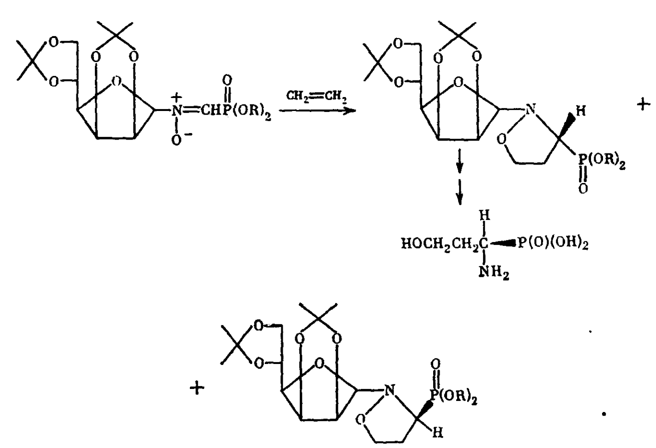
The aldimine obtained from aminomethylphosphonate can be alkylated by halogenoalkanes; the hydrolysis of the resulting compounds leads to the α-aminophosphonic acids Ala^P, Phe^P, and As-$^{\alpha-P}$:[178]



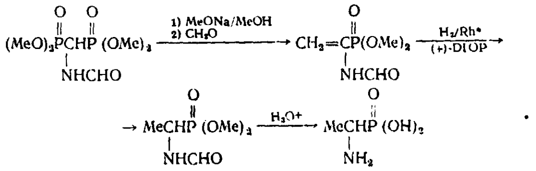
The oxazoline method of synthesis of α-aminoacids has been applied to the synthesis of the phosphonic analogues of derivatives of serine, the oxazolinylphosphonates necessary for this purpose being formed as a result of the addition of carbonyl compounds to isocyanomethylphosphonates:[179]



The cycloaddition of ethylene to C-dialkoxy-N-glycosylphosphonoylnitrones, which proceeds with appreciable stereoselectivity, has been used to synthesise laevorotatory phosphonic analogues of homoserine, aspartic acid, and asparagine:[180]



α-(*N*-Formylamino)vinylphosphonate, obtained by the Horner–Wittig reaction from *N*-formylaminomethylenediphosphonate and paraformaldehyde, gives rise to α-(*N*-formylamino)ethylphosphonate as a result of hydrogenation on a complex rhodium catalyst (Rh*) in the presence of the chiral ligand (+)-2,3-dihydroxy-2,3-*O*-isopropylidene-1,4-bis(diphenylphosphino)butane (DIOP). Hydrolysis of the product leads to the optically active (–)-α-aminoethylphosphonic acid (with an enantiomeric excess of 76%):[181]



$$\underset{NHCHO}{(MeO)_2\overset{O}{\overset{\|}{P}}CH\overset{O}{\overset{\|}{P}}(OMe)_2} \xrightarrow[\;]{1)\,MeONa/MeOH \atop 2)\,CH_2O} \underset{NHCHO}{CH_2{=}C\overset{O}{\overset{\|}{P}}(OMe)_2} \xrightarrow[(+)\text{-}DIOP]{H_2/Rh^*}$$

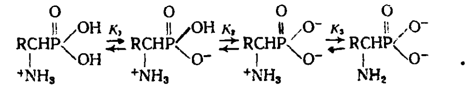
$$\rightarrow \underset{NHCHO}{MeCH\overset{O}{\overset{\|}{P}}(OMe)_2} \xrightarrow{H_3O^+} \underset{NH_2}{MeCH\overset{O}{\overset{\|}{P}}(OH)_2}\,.$$

Many aminophosphonic acids have been obtained by modifying particular functional groups present in the phosphonates. For example, the phosphonic analogue of arginine has been obtained from the phosphonic analogue of ornithine by converting the δ-amino-group into the guanidino-group.[182] Derivatives of β-aminoethylphosphonic acid have been obtained by reducing the nitro-group in β-nitroethylphosphonates[183,184] and the nitrile group in phosphonoacetonitriles.[185] Catalytic hydrogenation of α-hydroxy-β-nitroethylphosphonates has been used to obtain derivatives of β-amino-α-hydroxyethylphosphonic acid.[186,187] This acid is also formed on ammonolysis of oxiranylphosphonates.[188]

As can be seen from the foregoing, there is at present a fairly wide set of methods of synthesis of APA based both on the specific properties of individual phosphorus-containing reagents and on the application of the "standard" methodology for the synthesis of aminocarboxylic acids. Phosphorus analogues of many natural α-aminocarboxylic acids have been obtained by these methods. However, one should note that α-APA containing additional functional groups (analogues of serine, threonine, lysine, etc.) are still difficult to obtain and the phosphorus analogues of certain important natural aminoacids have not been described hitherto. The problem of the asymmetric synthesis of α-APA also remains urgent and requires new solutions.

III. THE PROPERTIES OF AMINOPHOSPHONIC, AMINOPHOSPHINIC, AND AMINOPHOSPHONOUS ACIDS

Aminophosphonic, aminophosphinic, and aminophosphonous acids are white high-melting crystalline substances, soluble in water and sparingly soluble in ethanol and other organic solvents. On recrystallisation from aqueous solvents, some of them are isolated as hydrates.[51,189] The potentiometric titration curves for aminophosphonic acids have three breaks corresponding to the three ionisation constants of these compounds:[129,190]



The ionisation constants and isoelectric points of valine and its phosphonic and phosphonous analogues are presented in Table 1.

Table 1. The ionisation constants and isoelectric points of valine and its phosphorus analogues.[88]

Acid	pK_1	pK_2	pK_3	p*I*
$\underset{NH_2}{Me_2CHCHCOOH}$	2.28	9.36	–	5.82
$\underset{NH_2}{Me_2CHCH\overset{O}{\overset{\|}{P}}(OH)_2}$	1.23	5.68	10.46	3.46
$\underset{NH_2}{Me_2CHCH\overset{O}{\overset{\|}{P}}}(H)(OH)$	1.19	7.79	–	4.49

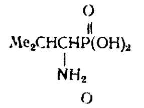
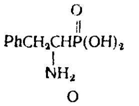
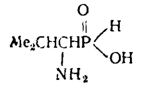
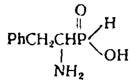
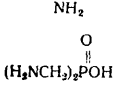
The ionisation constants of α-aminophosphonic acids in water[143,190] indicate the greater acidity of the phosphonic acid group in these compounds compared with the corresponding phosphonic acids themselves,[191] which is due to the influence of the amino-group. As was to be expected, aminophosphonic, aminophosphinic, and aminophosphonous acids have a zwitter-ionic structure, which has been confirmed by the NMR study of their aqueous solutions[88,192] and an X-ray diffraction study of crystalline specimens.[189]

Like aminocarboxylic acids, α-aminophosphonic acids are able to form complexes with many metal cations, in particular with Ni^{2+} and Cu^{2+}.[193] In their chelating capacity, α-aminophosphonic acids are close to aminocarboxylic acids and, with increase of the number of phosphono-groups in the molecule, the complex-forming capacity also increases, polyaminopolyalkylphosphonic acids being effective complexones.[194,195] Aminomethylphosphonic acid reacts with the Co^{2+} ion to form the compound $[Co(H_2NCH_2PO_3H_2)_2.2H_2O]H_2O$, which crystallises in the monoclinic system and is a coordination polymer produced as a result of the formation of –O–P–O bridge bonds between the cobalt atoms.[196]

The IR spectra of the APA and their esters have characteristic absorption bands due to the P=O (1150–1250 cm^{-1}), P–O–C (1040–1060, 1165 cm^{-1}), and $P–O^-$ (1000–1100 cm^{-1}) groups.[88,197] The IR spectra of aminophosphonous acids also contain the absorption band due to the P–H group (2300 to 2400 cm^{-1}).[88] The amino-group in free APA is protonated, as a result of which the IR spectrum exhibits broad absorption bands due to the $^+NH_3$ group (2000–3200 cm^{-1}, 1560 to 1600 cm^{-1}), which usually overlap in the region of approximately 3000 cm^{-1} with the absorption due to the stretching vibrations of the C–H and O–H bonds.[37,198] The IR spectra of APA esters show absorption bands due to the NH_2 group (3280–3380 cm^{-1}, 1500–1620 cm^{-1}).[66]

The ^{31}P NMR chemical shifts for certain APA and their esters are presented in Table 2. The table shows that these chemical shifts depend on the pH of the medium, which can be explained by the formation of protonated forms of these compounds in an acid medium and the deprotonated forms in an alkaline medium.[33,88,168,199]

Table 2. The chemical shifts and spin–spin coupling constants for the ^{31}P NMR spectra of certain aminophosphonic, aminophosphinic, and aminophosphonous acids.

Compound	$\delta(^{31}P)^*$, p.p.m. (solvent)	Refs.
 $\mathrm{Me_2CHCH(NH_2)P(O)(OH)_2}$	$+21.0$ (2N KOH) $+16.36$ (85% H_3PO_4)	[61] [134]
 $\mathrm{PhCH_2CH(NH_2)P(O)(OH)_2}$	$+21.2$ (2N KOH)	[177]
 $\mathrm{Me_2CHCH(NH_2)P(O)(H)OH}$	$+18.6$, J_{P-H} 540 Hz (D_2O) $+31.2$, J_{P-H} 501 Hz (NaOD)	[88] [88]
 $\mathrm{PhCH_2CH(NH_2)P(O)(H)OH}$	$+19.2$, J_{P-H} 543 Hz (D_2O) $+31.7$, J_{P-H} 513 Hz (NaOD) $+24.8$, J_{P-H} 574 Hz (DCl)	[88] [88] [88]
 $\mathrm{(H_2NCH_2)_2P(O)OH}$	$+29.77$ (D_2O) $+40.6$ (NaOH) $+20.36$ (HCl)	[168] [168] [168]
 $\mathrm{Me_2CHCH(NH_2)P(O)(OC_2H_5)_2}$	$+28.36$ (CH_2Cl_2) $+19.7$ (AcOH)	[140] [140]

*$\delta > 0$ when the signal is in a low field relative to the external standard—85% H_3PO_4.

α-Aminophosphonic, α-aminophosphinic, and α-aminophosphonous acids contain a chiral centre—the α-carbon atom—and exist in the form of two enantiomers. Almost all the methods of synthesis examined above lead to racemic mixtures with the exception of the instances of asymmetric synthesis where one of the enantiomers predominates in the product.[68,78–81,124,158,163,180,181] In order to obtain optically active α-APA, mixtures of diastereoisomers, formed on treatment of the racemate with an optically reactive reagent, are separated by repeated recrystallisation. The reagent of this kind most often employed is dibenzoyl-L-(+)-tartaric acid, which forms mixtures of diastereoisomeric salts on reaction with esters of α-aminophosphonic and the corresponding phosphinic acids. The (–)-diethyl ester of α-aminobenzylphosphonic acid with an optical purity in excess of 97%,[106,200] the (+)- and (–)-diethyl esters of the phosphonic analogue of phenylalanine, formed on hydrolysis of the enantiomeric Phe^P,[189] other optically active α-aminophosphonates,[25,201] and also the (+)-ethyl ester of α-aminobenzylphenylphosphinic acid[202] have been obtained in this way. On reaction with the diphenyl esters of α-aminophosphonic acids, the anhydride of dibenzoyl-L-(+)-tartaric acid gives rise to mixtures of diastereoisomeric amides (or imides), which afford optically active α-aminophosphonic acids after separation and hydrolysis. The enantiomers of the phosphonic analogues of alanine, valine, leucine, phenylalanine, phenylglycine,[203,204] and serine[41] have been synthesised by this procedure. The monoalkyl esters of *N*-acylated α-aminobenzylphosphonic acid have been separated into their enantiomers via the diastereoisomeric salts with *R*-(+)- and *S*-(–)-α-phenylethylamines [205] and (–)-ephedrine.[206] The (+)- and (–)-α-phenylethylamines have also been used to obtain optically active α-aminophosphonous acids.[88]

The acylation of the amino-group in racemic α-aminophosphonates by derivatives of optically active α-aminocarboxylic acids gives rise to diastereoisomeric phosphonodipeptides, which can be separated by chromatography on ion-exchange resins[200,207] or silica gel;[208] a method based on the separation by column chromatography for unprotected or fully protected phosphonodipeptides with subsequent acid hydrolysis of the resulting diastereoisomers has been proposed for the synthesis of optically active α-aminophosphonic acids.[203] The possibility of the enzymic separation of *N*-acyl derivatives of α-aminophosphonic acids has also been reported.[209]

The absolute configuration of certain optically active α-aminophosphonic acids has been determined by X-ray diffraction. The *S*-configuration of the chiral centre has been observed for (–)-Val^P and (–)-α-aminobenzylphosphonic acid;[78,79] (+)-Phe^P also has the *S*-configuration and the bond lengths and angles do not differ significantly from the usual values and are close to the analogous parameters of phenylalanine derivatives;[189] (+)-Ala^P likewise has the *S*-configuration.[210]

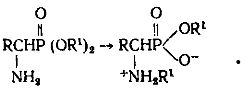
Comparative analysis of the NMR data and of the specific rotations of the glycosidic precursors made it possible to attribute the *R*-configuration to the laevorotatory enantiomers of the phosphonic analogues of homoserine, asparagine, and aspartic acid [(–)-Asp$^{\alpha-P}$].[180] From the chromatographic behaviour of diastereoisomeric phosphonodipeptides containing the *N*-terminal L-Phe residue and the P-terminal Leu^P, Met^P, and Phe^P residues, the *R*-configuration was also attributed to the laevorotatory enantiomers of these α-aminophosphonic acids.[208] The absolute configurations of a series of optically active α-aminophosphonic acids, namely *S*-(+)-Ser^P, *S*-(+)-aziridinylphosphonic acid, *S*-(+)-α-amino-β-chloroethylphosphonic acid, R-(–)-Phe^P, and R-(–)-Tyr^P, have been established by means of chemical correlation with α-aminophosphonic acids having known configurations.[201] The laevorotatory enantiomer of the phosphonous analogue of alanine has the *R*-configuration, because it is oxidised to R-(–)-Ala^P.[88]

The asymmetric esters of α-aminophosphonic acids contain two asymmetric centres, C_α and P, and exist in the form of diastereoisomers which are clearly distinguishable by the NMR spectra.[206,211,212] Mixtures of diastereoisomers are formed similarly in the case of α-aminophosphinic acid esters. It has been established by X-ray diffraction that the asymmetric centres of the (+)-isomer of ethyl α-aminobenzylphenylphosphinate have the absolute *R*(C_α), *S*(P)-configuration.[202]

1. Reactions of the Amino-group in Aminophosphonic, Aminophosphinic, and Aminophosphonous Acids

α-Aminophosphonic acids are protonated at the amino-group in acid media, but it is not possible to isolate the salts, in particular the hydrochlorides, in a pure state, since the ratio α-APA/HCl is greater than unity.[146] After prolonged heating of the hydrochlorides of aminophosphonic acids, hydrogen chloride is fully eliminated with formation of free aminophosphonic acids, which can be accounted for by the appreciable acidity of the phosphono-group.[18,129] α-Aminophosphonic acid esters form hydrochlorides,[103,197] picrates,[197] and acid oxalates[136,137,175] with characteristic melting points, which are used for their isolation, purification, and identification. Racemic α-aminophosphonates and the corresponding phosphinates react with optically active acids to form diastereoisomeric salts, which are used for their resolution into enantiomers.[25,106,189,200,201]

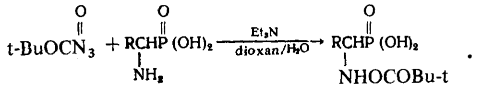
α-Aminophosphonic acids and their esters are alkylated at the amino-group on treatment with methyl iodide or dimethyl sulphate; exhaustive alkylation of α-APA leads to the formation of "phosphonobetaines".[213-215] The full esters of α-aminophosphonic acids are gradually converted into the monoesters even at room temperature:



$$RCH(NH_2)P(O)(OR^1)_2 \rightarrow RCH(\overset{+}{N}H_2R^1)P(O)(OR^1)O^- .$$

The rate of this process depends on the nature of the group R^1 and diminishes in the sequence Me > Et > n-Pr > iso-Pr.[107] The *N*-arylation of α-aminophosphonic acids by 1-nitro-9-phenoxyacridine has been described.[216]

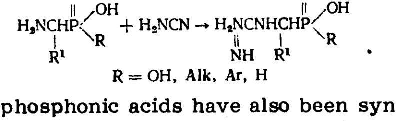
On interaction with an excess of acetic anhydride, α-aminophosphonic acid esters give rise to *N*-acetyl derivatives, while their reaction with benzoyl chloride or tosyl chloride in the presence of pyridine affords *N*-benzoyl and *N*-tosyl derivatives respectively.[217,218] *N*-Benzyloxycarbonyl derivatives of α-aminophosphonic acid esters have been obtained by the Schotten–Baumann acylation,[219] by reaction with *N*-(*O*-benzyloxycarbonyl) hydroxysuccinimide,[206] and by acylation with benzyloxycarbonyl chloride in chloroform in the presence of triethylamine.[220,221] On heating with acetic anhydride, the free α-aminophosphonic acids produce *N*-acetyl derivatives;[115,217] *N*-chloroacetyl,[215] *N*-benzoyl,[129,143,217] *N*-tosyl,[222] and *N*-benzyloxycarbonyl derivatives[222-224] of α-APA have been obtained by the Schotten–Baumann acylation with the corresponding acid chlorides in aqueous alkaline media. α-Aminophosphonic acids are formylated by 100% formic acid in acetic anhydride and are converted into *N*-trifluoroacetyl derivatives on interaction with trifluoroacetic acid anhydride.[141] On fusion with phthalic anhydride, *N*-phthaloyl derivatives of α-aminophosphonic acids are formed.[215,222] The interaction of α-aminophosphonic acids with t-butoxycarbonyl azide in aqueous dioxan in the presence of triethylamine leads to the formation of *N*-t-butoxycarbonyl derivatives:[225]



$$t\text{-BuOC(O)N}_3 + RCH(NH_2)P(O)(OH)_2 \xrightarrow[\text{dioxan/H}_2\text{O}]{\text{Et}_3\text{N}} RCH(NHCOBu\text{-}t)P(O)(OH)_2 .$$

The amino-group in α-aminophosphonic acids[226] and their esters[227] condenses with aldehydes to form the corresponding aldimines.

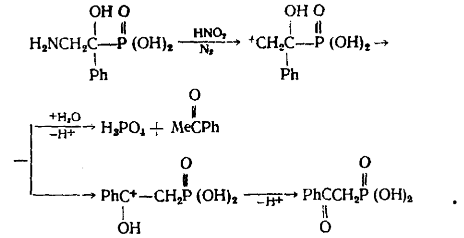
On interaction with cyanamide, α-aminophosphonic, α-aminophosphinic and α-aminophosphonous acids give rise to α-guanidinophosphonic,[228] α-guanidinophosphinic,[229] and α-guanidinophosphonous[228] acids:



$$H_2NCH(R^1)P(O)(OH)R + H_2NCN \rightarrow H_2NC(=NH)NHCH(R^1)P(O)(OH)R .$$

R = OH, Alk, Ar, H

α-Guanidinophosphonic acids have also been synthesised by the reaction of α-aminophosphonic acids with *S*-ethylisothiourea.[230] α-Aminoalkylphosphonates can be oxidised to the corresponding α-nitroalkylphosphonates.[231] The diazotisation of aminophosphonic and aminophosphinic acids leads to the formation of carbonium ions, which fragment or rearrange depending on their structure:[51,198,232]

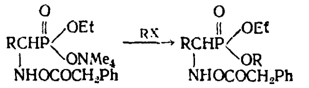


$$H_2NCH_2C(OH)(Ph)P(O)(OH)_2 \xrightarrow[N_2]{HNO_2} {}^+CH_2C(OH)(Ph)P(O)(OH)_2 \rightarrow$$
$$\xrightarrow[-H^+]{+H_2O} H_3PO_4 + MeC(O)Ph$$
$$\rightarrow PhC^+(OH)-CH_2P(O)(OH)_2 \xrightarrow{-H^+} PhC(O)CH_2P(O)(OH)_2 .$$

Like aminocarboxylic acids, α-APA produce a characteristic purple-violet colour on interaction with ninhydrin, which is used for their detection.[15,88,129,233]

2. Reactions of the Phosphorus-containing Fragments of Aminophosphonic, Aminophosphinic, and Aminophosphonous Acids

The di- and mono-esters of α-aminophosphinic acids can be obtained by the esterification of the phosphono-group in *N*-protected α-aminophosphonic acids. The dimethyl esters are formed when *N*-acylated *N*-aminophosphonic acids are treated with diazomethane.[222,225] The interaction of diazomethane with the monoesters of *N*-acylaminophosphonic acids affords asymmetric esters.[205,211,222,234,235] Diazoethane[205] and diphenyldiazomethane[236,237] interact with *N*-acylated α-aminophosphonic acids and their monoesters like diazomethane. In the presence of [tritiated? (Ed.of Translation)] ultra-heavy water, diazoethane esterifies the monoethyl esters of *N*-benzyloxycarbonylaminophosphonic acids with formation of tritium-labelled diethyl esters.[238] Ethyl orthoformate is used to introduce the ethyl group in the synthesis of diethyl and asymmetric alkyl ethyl esters.[206,211,224,234] Asymmetric ethyl methyl, benzyl ethyl, and cyanomethyl ethyl esters have been obtained by the reaction of the tetramethylammonium salts of the monoethyl esters of *N*-acylated α-aminophosphonic acids with corresponding alkylating agents:[239]

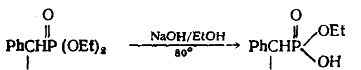


$$RCH(NHCOCH_2Ph)P(O)(OEt)(ONMe_4) \xrightarrow{RX} RCH(NHCOCH_2Ph)P(O)(OEt)(OR)$$

$RX = MeI, PhCH_2Br, NCCH_2OSO_2Ph$.

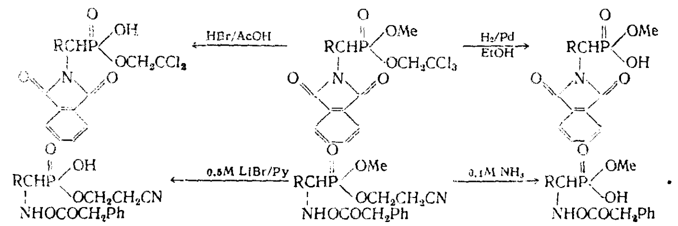
N-Acylated α-aminophosphonic acids give rise to monoesters on esterification with hydroxy-compounds in the presence of pyridine in trichloroacetonitrile[211,234,235,240,241] and on condensation with alcohols in the presence of dicyclohexylcarbodiimide (DCC).[141,242]

Another approach to the synthesis of the monoesters of α-aminophosphonic acids involves the partial hydrolysis of the diesters. When the diethyl ester of the phosphono-analogue of phenylalanine was heated with 80% acetic acid, the monoethyl ester was obtained in 10% yield.[141] The alkaline hydrolysis of *N*-acylated dialkyl aminophosphonates proceeds more successfully:[221,243]



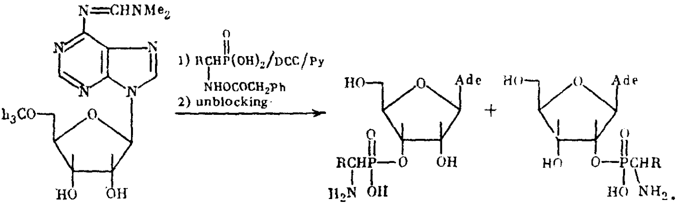
$$PhCH(NHCOCH_2Ph)P(O)(OEt)_2 \xrightarrow[80°]{\text{NaOH/EtOH}} PhCH(NHCOCH_2Ph)P(O)(OEt)(OH) .$$

In many instances, the monoesters of *N*-acylated α-aminophosphonic acids can be obtained by the non-hydrolytic cleavage of the diesters by treating the latter with reagents such as boron tribromide in methylene chloride, lithium bromide in pyridine, sodium thiophenoxide in ethanol, or a 45% solution of HBr in glacial acetic acid.[244] The monoesters of *N*-acylated α-aminophosphonic acid are also formed when the ester groups in asymmetric diesters are removed selectively:[206,211,234,235]



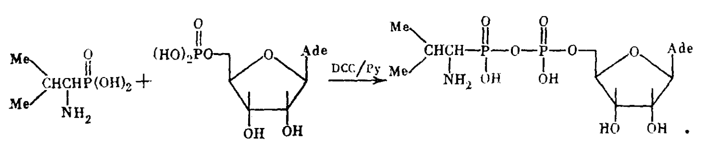
The monoethyl ester of the phosphonic analogue of valine has been obtained by heating the hydrochloride of its diethyl ester.[141] The monoethyl ester of *N*-phthaloylaminomethylphosphonic acid is formed on hydrolysis of the corresponding chlorophosphonate obtained on treatment of the diethyl ester with phorphorus pentachloride.[243]

α-Aminophosphonic acids have been made to react with nucleosides and nucleotides. The *N*-benzyloxycarbonyl derivatives of $\mathrm{Ala^P}$ and $\mathrm{Phe^P}$ (in the form of pyridinium salts) condense with the free 2'- or 3'-hydroxy-groups of *N*-dimethylaminomethylene-5'-*O*-trityladenosine in the presence of DCC. After the removel of the protecting groups and chromatographic purification on DEAE-cellulose, adenosine derivatives phosphorylated in the 2'- and 3'-position by the corresponding α-aminophosphonic acids were obtained in 20–38% yield:[245]



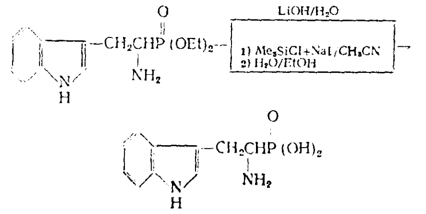
R = Me, PhCH$_2$; Ade = 9-adeninyl.

N-Benzyloxycarbonyl-$\mathrm{Ala^P}$ interacts with 2',3'-*O*-isopropylideneuridine or the corresponding adenosine derivative in the presence of mesitylenesulphonyltriazole as the condensing agent with formation of the corresponding 5'-*O*-(α-aminoethylphosphonoyl) ribonucleosides in 40–50% yield.[246] When 2,4,6-triisopropylbenzenesulphonyl chloride is used as the condensing agent, the yield of the phosphorylated ribonucleosides is low; only traces of the target product are formed in the presence of DCC.[246] $\mathrm{Val^P}$ condenses with adenosine monophosphate (AMP) in the presence of DCC to form a mixed anhydride (in 20% yield):[142]



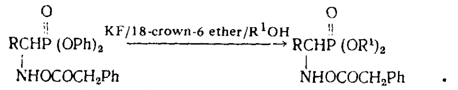
The mixed anhydrides of AMP with $\mathrm{Phe^P}$ and $\mathrm{Met^P}$ were obtained analogously (in yields of 17–24%).[247] In the condensation of the trioctylammonium salts of AMP with the imidazolides of α-aminophosphonic acids, the yield of the corresponding mixed anhydrides is somewhat higher (26–35%). The highest yields of the mixed anhydrides (50–62%) were attained in the reaction of *N*-protected α-aminophosphonic acids with AMP imidazolides.[247] In the condensation of AMP with the monoethyl ester of the phosphonic analogue of valine, the phosphono-group of the latter was activated by treatment with phosgene; the yield of the condensation products was 45%.[247] The chemical and enzymic syntheses of the mixed anhydride of β-aminoethyl phosphonic acid and cytidine 5'-phosphate have also been described.[248]

The esters of α-aminophosphonic and the corresponding phosphinic acids are converted into the free acids usually by hydrolysis in acid media. The rate of hydrolysis depends on the nature of the *O*-alkyl (*O*-aryl) groups split off (for example, in acid hydrolysis the *C*-isopropyl groups are eliminated much more readily than the *O*-ethyl groups[109]) and the character of the acid employed (the rate of hydrolysis falls in the sequence HI > HBr > HCl [143]). In those cases where the aminophosphonate is unstable in an acid medium, the hydrolysis is carried out with alkalies[136] or the compound is *O*-dealkylated by treatment with halogenosilanes in acetonitrile:[136,159]



Phenyl,[249] benzyl,[250] diphenylmethyl,[236,237] and trichloroethyl[211] P-ester groups can be removed by catalytic hydrogenolysis. The diphenylmethyl group is eliminated also on refluxing with ethanol or on treatment with trifluoroacetic acid at room temperature.[237] The *p*-methylbenzyl group is eliinated by treatment with 98% formic acid.[251] *OO*-Disilylaminophosphonates are converted into free aminophosphonic acids after prolonged heating with alcohols or a water–alcohol mixture.[80,82] The diethyl esters of *N*-alkylaminophosphonic acids, which are extremely resistant to hydrolysis by aqueous solutions of acids and bases, have been converted into the free acids by treatment with dry hydrogen chloride at an elevated temperature.[197,152]

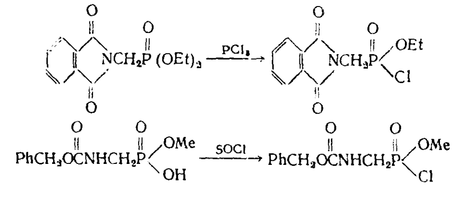
The diphenyl esters of *N*-acylated α-aminophosphonic acids can be converted into the dialkyl esters by transesterification in the fluoride–crown ether–alcohol system:[204,253]



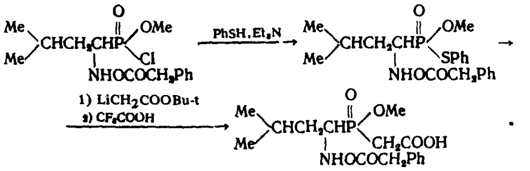
$$\underset{\mathrm{NHCOCH_2Ph}}{\mathrm{RCH}}\overset{\mathrm{O}}{\mathrm{P}}\mathrm{(OPh)_2} \xrightarrow{\mathrm{KF/18\text{-}crown\text{-}6\ ether/R^1OH}} \underset{\mathrm{NHCOCH_2Ph}}{\mathrm{RCH}}\overset{\mathrm{O}}{\mathrm{P}}\mathrm{(OR^1)_2}$$

R = Me, Et, Pr, Bu, CH$_2$CH=CH$_2$

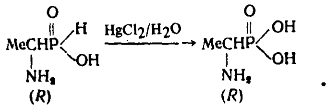
The *N*-protecting groups and peptide bonds are not involved in such transesterification, which makes it possible to employ this process for the modification of phosphonopeptides.[249] *N*-Protected aminophosphonates can be converted into the corresponding aminophosphonochloridates by treatment with phosphorus pentachloride[243,250,254] or thionyl chloride:[220,221]



These phosphonochloridates interact readily with nucleophiles and are used for the synthesis of phosphonopeptides and other derivatives of aminophosphonic acids. For example, the α-aminophosphonic acid $\mathrm{Leu^P}$ has been converted into the α-aminophosphinic acid with a carboxymethyl substituent at the phosphorus atom ($\mathrm{Leu}^{P-CH_2COOH}$) in accordance with the following scheme:[255]

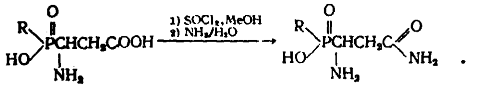


α-Aminophosphonous acids are oxidised with mercury(II) chloride or bromine water to the corresponding α-aminophosphonic acids with retention of the configuration of the chiral α-carbon atom:[86,88,123]



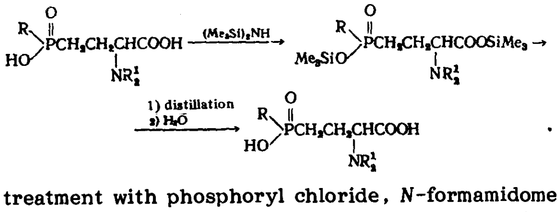
3. Reactions of Other Groups Present in Aminophosphonic and Aminophosphinic Acids

The carboxy-group in carboxylated aminophosphonic and aminophosphinic acids can be esterified without involving the phosphorus-containing fragment.[33,42,199] Such esterification of the carboxy-group in $\mathrm{Asp}^{\alpha-P}$ with subsequent ammonolysis has been used to obtain the phosphonic and phosphinic analogues of asparagine:[130,131]

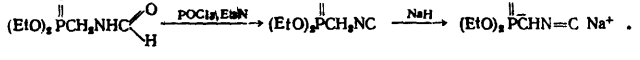


R=OH, Me, Et

In the presence of diazabicycloundecene and alkyl halides or diazomethane the carboxy- and phosphono-groups in carboxylated aminophosphonic acid are esterified simultaneously.[163] When aminophosphonic and aminophosphonic acids are heated with an excess of hexamethyldisilanzane, the trimethylsilyl derivatives are formed.[100] A method has been proposed for the purification of APA, consisting in their silylation with subsequent distillation and removal of silyl groups by hydrolysis or alcoholysis:[15,256]

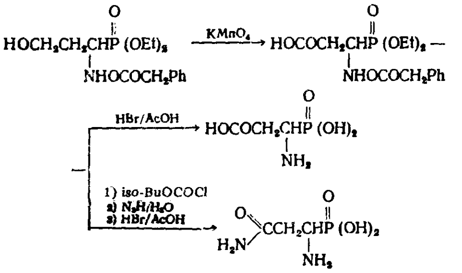


On treatment with phosphoryl chloride, *N*-formamidomethylphosphonates are converted into isocyanomethylphosphonates containing the readily metallated methylene group:[75]

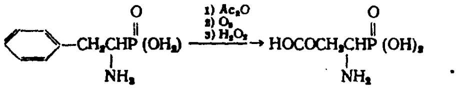


The interaction of the resulting anion with electrophiles leads to the heterocyclic P–C–N systems: the esters of oxazolylphosphonic acids (reactions with acid chlorides and carbonyl compounds) and the ester of mercaptothiazolylphosphonic acid (reaction with carbon disulphide).[75,257,258] Analogous reactions have been described for *N*-formamidomethylphosphinates.[15]

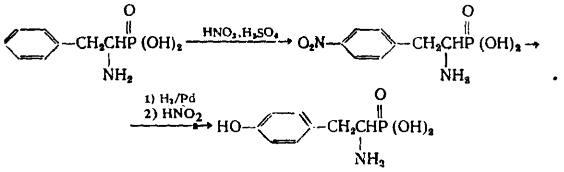
On treatment with a mixture of acetic and hydrobromic acids, the phosphonic analogues of serine and isoserine give rise to the O-acetyl derivatives without affecting the amino-group.[159] The oxidation of the β-hydroxymethylene fragment of the phosphonic analogue of homoserine has been used to synthesise the phosphonic analogues of asparagine (Asn^{P}) and aspartic acid ($\mathrm{Asp}^{\alpha-P}$):[180]



The ozonolysis of the phosphonic analogue of phenylalanine followed by oxidative treatment results in the decomposition of the benzene ring and the formation of the phosphonic analogue of aspartic acid ($\mathrm{Asp}^{\alpha-P}$):[201]



The phosphonic analogue of phenylalanine has been converted into the phosphonic analogue of tyrosine via the following scheme:[201]



Since these reactions do not involve the chiral centre, they have been used to determine the absolute configurations of the optically active aminophosphonic acids $\mathrm{Asp}^{\alpha-P}$, $\mathrm{Asn}^{\alpha-P}$, Phe^{P}, and Tyr^{P}.[180,201]

As can be seen from the foregoing, the chemistry of APA constitutes at the present time an independent chapter in the chemistry of organophosphorus compounds with its own tasks and approaches to their solution. Both traditional methods of synthesis of OPC and the "phosphorus" versions of the classical methods of synthesis of aminocarboxylic acids are widely used in the chemistry of APA. The advances in the chemistry of APA have made available a wide range of phosphorus analogues of natural aminoacids, although many problems, for example the synthesis of polyfunctional and optically active APA, have still not had optimal solutions.

A characteristic feature of this field of HPC is that it adjoins closely bio-organic chemistry and biochemistry. This is related not only to the structural similarity of the aminoacids and APA but also to the existence of natural APA, which confirms their definite biological role. The development of research into the field of APA has already led to the creation of highly active herbicides (glyphosphate, phosphinothricin) and promising medicinal drugs (the antibiotic alaphosphin).

Presumably further studies in the field of APA will involve primarily the development of methods of synthesis of APA and the complex analogues of the most important biologically active natural products containing APA fragments. Secondly, they will involve the wide-scale employment of these compounds in bio-organic research and, finally, they will be associated with the search for new substances of practical use in medicine and agriculture.

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Platinum(II) Complexes of Purine and Pyrimidine Bases and Their Nucleosides

A.I.Stetsenko, K.I.Yakovlev, and S.A.D'yachenko

The results of studies on the synthesis, structure, and physicochemical properties and reactivities of platinum(II) complexes of purine and pyrimidine bases and their nucleosides, carried out mainly during the last decade, are summarised. Attention is directed to the characteristic features of these compounds as ambident and bridging ligands. The methods of study are characterised and the influence of coordination on the physicochemical characteristics of the purine and pyrimidine ligands and the effect of the mutual influence of the ligands in the platinum(II) complexes are analysed. The data concerning the ways in which the purine and pyrimidine ligands are bound in the platinum(II) complexes are compared with the manifestation of the antitumour activity by these complexes.
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I. INTRODUCTION

The antiblastoma activity of *cis*-dichlorodiammineplatinum-(II), i.e. *cis*-[Pt$(NH_3)_2Cl_2$] (*cis*-DDP) was discovered in 1969.[1] At the present time this compound is used as an effective antitumour agent with a broad spectrum of activity.[2,3] Under the names "Platind", "*cis*-Platina", Neoplatin", and "Platidiam", *cis*-DDP is manufactured in the USA, England, Czechoslovakia, Finland, and certain other countries.

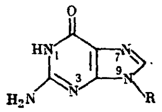
Other platinum complexes are also being vigorously investigated in the search for active water-soluble compounds with a low toxicity. Complexes of chelating dicarboxylate dianions having the *cis*-structure and constituting the so-called second generation of cytostatic platinum(II) complexes are in the stage of clinical tests. They include cyclobutane-1,1-dicarboxylatodiammineplatinum(II), a series of platinum(II) complexes of diaminocyclohexane (malonates and substituted malonates as well as 4-carboxyphthalate), and a platinum(IV) complex—*cis*-dichlorodiisopropyl-*trans*-dihydroxoplatinum-(IV).[4-7] The antitumour activity of the platinum complexes depends on many factors—the charge on the complex, the degree of oxidation of the central atom, the nature of the neutral and acido-ligands, and the kinetic and thermodynamic stability of the complexes.[4] One of the main factors is the geometrical configuration of the complexes: only the *cis*-isomers are active, the *trans*-isomers being inactive.

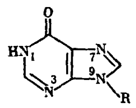
The mechanism of the antitumour action of the platinum complexes has so far been inadequately investigated. It has been established that the active complexes inhibit the synthesis of DNA *in vitro* and *in vivo* via reactions with heterocyclic DNA bases.[8-13] Among the DNA bases, the purine base guanine and the pyrimidine base cytosine show the greatest tendency to react with *cis*-DDP.[14-19] The specific action of *cis*-DDP on tumour cells is caused both by the faster division of these cells compared with normal cells and by the fact that the damage induced by *cis*-DDP is made good faster in normal cells than in tumour cells.[12]

cis-DDP can interact with DNA bases in different strands of the double helix, effecting the so-called intercross-linking,[20-22] for example, with the complementary bases—guanine and cytosine. However, this type of linkage is not dominant, since only 1% of the total amount of the platinum bound to DNA participates in intercross-linking.[23,24] The binding of *cis*-DDP by the molecules of the bases of a single DNA strand, the so-called intracross-linking, is more probable.[25-27] Nor can one rule out also the reactions of *cis*-DDP with the same DNA base via a chelating mechanism.[28-31] Intracross-linking can in fact explain the dependence of the antitumour activity on the geometrical configuration of the complexes: (1) the distance between the planes of the bases in DNA is 3.4 Å, which corresponds to the distance between the chlorine atoms in DDP (3.3 Å) and differs from the distance in the *trans*-isomer (4.66 Å); (2) only the *cis*-isomers are capable of forming chelate bonds. Apart from the direct interaction with DNA, the active complexes can influence the bond between DNA and proteins.[32-34]

II. METHODS OF STUDY, SYNTHESIS, STRUCTURE, AND PROPERTIES OF PLATINUM(II) COMPLEXES OF PURINE BASES AND THEIR NUCLEOSIDES

The purine bases with R = H include guanine (Gu) (I), hypoxanthine (Hyp) (II), and adenine (Ad) (III). Their nucleosides (with R = β-D-ribofuranosyl) are guanosine (Gua), inosine (Ino), and adenosine (Ado).


(I)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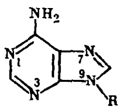

(III)

The presence of several endocyclic nitrogen atoms and also of the potentially electron-donating exocyclic groups and atoms (NH_2, O) is responsible for the ambident nature of the ligands and complicates the determination of the structure of their complexes. Physical, mainly spectroscopic, methods are used for this purpose: UV, IR, and Raman spectroscopy, X-ray electronic spectroscopy, circular dichroism, fluorescence analysis, atomic absorption, and, to the greatest extent, ^1H, ^{13}C, ^{15}N, and ^{195}Pt ($I = 1/2$) microwave spectroscopy. The complexity of the IR spectra of the ligands and the low sensitivity of the UV spectra to changes in the type of bond limit the application of these methods to the determination of the structures of the complexes. The NMR methods are most informative and unambiguous. In many studies spectroscopic methods have been used to investigate the formation of complexes between platinum(II) and purine and pyrimidine bases in solutions. However, under these conditions there is a possibility of the existence of a series of complexes. More definite information about the compositions and structures of the complexes can be obtained by means of spectroscopic study of the complexes isolated. X-Ray diffraction studies lead to final conclusions about the structures of the complexes, but they cannot always be carried out owing to the difficulty of growing single crystals. Potentiometric titration with alkali is used to detect protonated NH groups in the coordinated ligands, to characterise the influence of coordination on the acidity of the ligands, and to investigate the state of the complexes in different media—pH and [Cl^-] determinations. The conductimetric method is used to study the kinetics of the substitution of chloride ions in the reactions of *cis*-DDP with purine and pyrimidine bases and their nucleosides. The NMR methods play the main role in the determination of the structures of the complexes. Here we shall indicate in greater detail the possibility of the use of proton magnetic resonance (^1H NMR). Comparison of the ^1H NMR spectra of free and coordinated ligands in D_2O can yield information about the non-labile protons [for example H(2) and H(8) in the adenosine molecule]. Coordination induces changes in the ^1H NMR spectra of the ligand. As a consequence of the decrease of electron density on formation of the donor–acceptor bond, the deshielding of the proton near the electron-donating atom and the downfield shift of its signal are observed. Furthermore, owing to the spin–spin coupling with the ^{195}Pt magnetic nucleus (nuclear spin $I = 1/2$), the signal of the nearest proton becomes a triplet with the intensity ratios 1:4:1 in conformity with the content of the ^{195}Pt isotope in natural platinum (34%). The spin–spin coupling constant $J_{^{195}Pt-^1H}$ depends on the distance between the ^1H and ^{195}Pt nuclei: thus, in the platinum(II) complexes with the thymine anion, we have $^3J = 38$ Hz, $^4J = 4–15$ Hz, and $^5J \cong 0$. The study of the ^1H NMR spectra in DMSO-d_6 makes it possible to characterise also the distance between the labile protons of the NH_2, OH, and SH groups in the coordinated ligands.

Examples of the application also of other microwave spectroscopic methods to the study of the structures of the platinum(II) complexes of purine and pyrimidine bases will be given below.

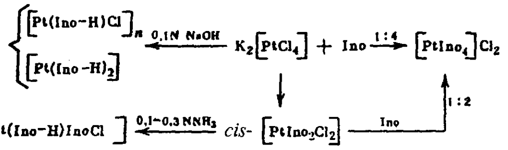
1. Platinum(II) Complexes of 6-Oxopurines and Their Nucleosides

Since *cis*-DDP is bound preferentially by the guanine in DNA, the interaction of guanine and guanosine with platinum(II) complexes has been investigated in most studies. Fewer studies have been devoted to the reactions with their antimetabolites—hypoxanthine and inosine. Guanine, hypoxanthine, and their nucleosides can be coordinated both in the form of neutral molecules and in the form of anions via different electron-donating atoms. There is a possibility of the following main types of coordination under these conditions: (a) monodentate—via the N(7), N(1), and N(9) heteroatoms (for the bases); (b) bidentate—via the N(7) and O(6) atoms; (c) bridged—with participation of the N(7) and N(1) or O(6) atoms.

(a) The Monodentate Type of Bond

The interaction of *cis*-DDP and *trans*-$[Pt(NH_3)_2Cl_2]$ with guanosine and inosine in solutions at different pH has been investigated by a differential spectrophotometric method.[13] It has been shown that the *cis*- and *trans*-isomers react with oxopurines in the same way, the latter being coordinated as monodentate species. At low pH, the bond is formed via the N(7) atom, while at high pH (pH > 9) it is formed via the deprotonated N(1) atom. The conclusion that this type of binding obtains has been confirmed by data for 7- and 1-methyl-substituted inosine and guanosine. The bonding of platinum(II) via N(7) has been established spectrophotometrically also for hypoxanthine.[35,36] However, the spectrophotometric method, especially when applied to solutions containing mixtures of products, cannot provide an exact answer about the ligand binding site. Studies in which the complexes are isolated are more promising. Platinum complexes of different types have been obtained with guanosine and inosine—neutral, cationic, and anionic with different numbers of purine molecules. The reaction of nucleosides with *cis*-$[Pt(NH_3)_2Cl_2]$ and $[PtenCl_2]$ (en = ethylenediamine) lead to the formation of mixed tetrammines having the composition $[PtA_2L_2]Cl_2$, where L = guanosine, inosine, and xanthine.[37] The reactions of $K_2[PtX_4]$ with nucleosides for a nucleoside to platinum ratio of 2, are accompanied by the formation of the *cis*-nonelectrolytes $[PtL_2X_2]$ (X = Cl or Br; L = Ino or Gua).[38] When the ratio is unity, the anionic complexes $K[PtLCl_3]$ are formed.[39] Cationic complexes with four nucleoside molecules have been isolated—$[PtIno_4]Cl_2$, $[PtGua_4]Cl_2$, and *cis*-$[PtIno_2Gua_2]Cl_2$.[40,41] All these compounds contain nucleoside molecules bound as monodentate species.

The reactions of inosine with platinum(II) complexes can be represented by the scheme



The coordination site in inosine has been determined by ^1H NMR. The signal of the H(8) proton in the ^1H NMR spectra of the compounds isolated by Kong and Theophanides[37] shifted downfield by 0.8 p.p.m. and that of the H(2) proton shifted by only 0.4 p.p.m. The H(2) signal in the spectra of the complexes remained as a singlet, while the H(8) signal was a triplet as a result of spin–spin splitting by the ^{195}Pt nucleus. These data enabled the authors to conclude that inosine is linked to platinum(II) via N(7). A similar type of bonding occurs also in other platinum(II) complexes with inosine and guanosine coordinated as monodentate species.[38–41] The ^1H and ^{13}C NMR methods, with the aid of which the occurrence of Pt–N(7) coordination was demonstrated,[2] were used to determine the donor atom of guanosine:

The H(8) signal is a triplet with $^3J[^{195}Pt - ^1H(8)] = 24$ Hz; in the ^{13}C NMR spectrum, $\Delta\delta[C(5)]$ and $\Delta\delta[C(9)]$ exceed on coordination the changes in the chemical shifts of signals due to other carbon atoms. X-Ray diffraction studies confirmed the monodentate mode of binding of guanosine and inosine via the N(7) atom in the complexes $[Pt(NH_3)_2Gua_2].Cl_{3/2}(ClO_4)_{1/2}$,[42] $[PtenGua_2]Cl_{3/2}I_{1/2}.2H_2O$,[43] and $[PtdienGua].(ClO_4)_2$ (dien = diethylenetriamine).[44] The same type of binding has been observed in the complexes of 9-methylguanine $[Pt(9\text{-}CH_3Gu)_4]Cl_2$ [45] and with the inosine nucleotide $[Pt(NH_3)_2(5'\text{-}IMP)_2]$ (5′-IMP = inosine 5′-monophosphate).[29]

Among the platinum(II) complexes with monodentate coordination of 6-oxopurines, almost no isomeric triammines of the type $[PtA_2LCl]Cl$, where A = NH_3 or ½en and L = Gu, Gua, Hyp, or Ino, have been isolated. Complexes of this type can be formed in the first stage of the interaction of DDP with DNA bases. They are of interest as objects to be used in tests for antitumour activity, since they contain one labile Cl^- ion together with the molecule of a lipophilic ligand and are readily soluble in water. The isomeric triammine complexes $[Pt(NH_3)_2LCl]Cl$ and *cis*-[PtenLCl]Cl (L = inosine or hypoxanthine) have been synthesised[46,47] by treating the isomeric non-electrolytes $[Pt(NH_3)_2Cl_2]$ and *cis*-$[PtenCl_2]$ with inosine or hypoxanthine in 1:1 proportions. The type of ionic decomposition and the inner-sphere location of the chloride ions have been established conductimetrically (Λ = 110–120 Ω^{-1} cm^2 mol^{-1}) and by IR spectroscopy $\nu(Pt-Cl)$ = 328–337 cm^{-1}. The $\nu(C=O)$ frequency changes little on coordination. The acid properties of the complexes and their hydrolytic stability have been investigated. Coordination leads to an appreciable intensification of the acid properties of inosine: the pK_a of free inosine is 8.9 [dissociation of N(1)H], while for certain isomeric triammines $[Pt(NH_3)_2InoCl]Cl$ the pK_a is 7.18 (*trans*-form) and 7.85 (*cis*-form) at an ionic strength of 0.3 (0.3 M KCl). Isomeric complexes of the tetrammine type, namely $[Pt(NH_3)_2.Ino_2]Cl_2$ and *cis*-$[PtenIno_2]Cl$, have been isolated and their acid properties have been investigated. The tetrammine complexes exhibit the properties of weak dibasic acids with similar dissociation constants: the pK_a^1 and pK_a^2 are 7.00 and 9.1 for the *cis*-form and 6.65 and 8.0 for the *trans*-form. The lower acidity of the *cis*-isomer reflects the greater *trans*-influence of NH_3 compared with inosine.

In relation to hydrolysis, the *cis*-triammine $[Pt(NH_3)_2.InoCl]Cl$ is less stable: the stability constant (0.1 M KNO_3, 25 °C) is 7.1 × 10^2 litre mol^{-1}, while the value for the *trans*-form is 1.4 × 10^3 litre mol^{-1}.[46,47] The same behaviour has been observed also for isomeric adenosine-containing triammines. Apparently the disposition of the cumbersome nucleoside molecule next to the chlorine ion decreases the stability of the Pt–Cl bond.

It is noteworthy that the synthesis of the triammines involves certain difficulties as a consequence of the possible admixture of complexes of the tetrammine type. These compounds are obtained more readily when substituted ligands are employed. Thus a chloride complex of N^2N^2-dimethyl-9-methylguanine of the triammine type has been isolated. Investigation of its geometry made it possible to attribute a smaller structural *trans*-effect to the N(7)-coordinated purine base compared with the Cl^- ion; the length of the Pt–N bond along the *trans*-coordinate $H_3N-Pt-Cl$ exceeds by 0.3 Å the length of the bond along the *trans*-coordinate H_3N–Pt–purine.[48]

On the basis of the available data, it can be regarded as established that the preferred site where guanosine, inosine, and hypoxanthine are bound to the central platinum(II) is the N(7) atom despite the fact that its basicity is extremely low {pK_b[N(7)] is 11.9 for Gua, 12.1 for Hyp, and 13.0 for Ino}, while the capacity of N(1)H for acid dissociation is appreciable {pK_a[N(1)H] is 8.7 for Ino, 8.8 for Hyp, and 9.2 for Gua},[49] so that it would seem that anionic complexes involving the substitution of the N(1)H proton should be formed rather than complexes with neutral nucleosides. Apparently the basicity of the N(7) nitrogen atom and the acidity of the N(1)H group are not factors determining the stability of the bond between nucleosides and the acid $[Pt(NH_3)_2]^{2+}$, which is much softer than the proton.

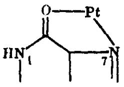
The coordination of guanosine via the N(7) atom in a neutral medium is characteristic also of another "soft" acid, namely CH_3^+Hg.[49]

The monodentate coordination of guanine via the N(7) atom is observed also in reactions of *cis*-DDP with DNA involving the intrastrand binding of *cis*-DDP to the N(7) atoms of neighbouring guanine molecules.[50–52]

In an alkaline medium, one may expect the binding of $Pt(NH_3)_2^{2+}$ and CH_3^+Hg to nucleosides as a result of the dissociation of the proton from N(1)H. The water-insoluble non-electrolytes $[Pt(Ino - H)_2]$ and $[Pt(Gua - H)_2]$,[38] isolated under these conditions, are polymers according to Raman and spectroscopic and ^1H NMR data[53,54] and contain bridging nucleoside anions linked to platinum(II) atoms not only via the deprotonated N(1)H group but also via coordination involving the N(7) atom. The monodentate binding of nucleosides via the protonated N(1)H group is not characteristic of platinum(II) complexes. Only when the N(7) and N(9) atoms in 7,9-dimethylguanine and 7,9-dimethylhypoxanthine are blocked by a methyl group, is it possible to achieve the monodentate coordination of guanine and hypoxanthine via the N(1)H groups. Thus studies have been made of the crystal structures of the following complexes which have been isolated: $[Ptdien7,9\text{-}(CH_3)_2Hyp](PF_6)_2$, $\{Pten[7,9\text{-}(CH_3)_2Hyp]_2\}(PF_6)_2$, and $\{Pt(NH_3)_2[7,9\text{-}(CH_3)_2Hyp]_2\}(NO_3)_2.2H_2O$.[55,57] These complexes are of interest also because their structures are to some extent analogous to those of platinum(II) complexes of cyclic amides—α-pyrrolidinone and α-pyridone,[58,59] containing the NHCO fragment.

(b) Bidentate Binding

The bidentate binding of 6-oxopurines and their nucleosides to platinum(II) of the N(7)–O(6) chelate type has been the subject of numerous discussions and has still not been demonstrated directly by X-ray diffraction. A chelate of this type is possible only for the *cis*-isomer.

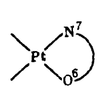


Since only the *cis*-isomer exhibits antitumour activity, many investigators see the cause of the difference between the activities of the $[Pt(NH_3)_2Cl_2]$ isomers in the fact that the *cis*-isomer forms a perfect chelate with the guanine of DNA, while the *trans*-isomer does not.[29,30,31,38,60,61]

In order to model the formation of this type of chelate in the interaction of DDP with DNA, a study has been made of the reaction of DDP with 6-oxopurines. The compounds isolated, whose composition corresponds formally to the bidentate binding of 6-oxopurines and their nucleosides, such as *cis*-$[PtA_2L]^{2+}$ and *cis*-$[PtA_2(L - H)]^+$, where $(L - H)^-$ is the ligand anion, as well as the complexes formed in solutions have been investigated. The following structural formulae can be proposed for the complexes having this composition.

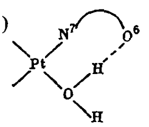
Monomeric complexes:

(a)



direct bidentate chelate bond

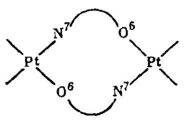
(b)



indirect chelation via the H bond between the O(6) atom and the proton of the coordinated water molecule.

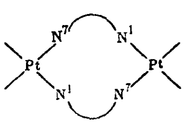
Dinuclear and polynuclear complexes with a bridge bond,

(c)



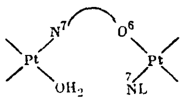
N(7)–O(6) bridge

(d)



N(7)–N(1) bridge

(e)



N(7)–Pt–O(6) bridge with monodentate H_2O and 6-oxopurine molecules.

Analogous bond types have been postulated also for coordinated 6-oxopurine anions. A direct answer to the question concerning their structure can be obtained by the X-ray diffraction method, but this is not always possible owing to the difficulty of isolating crystals suitable for analysis by X-ray diffraction. The possibility of chelation has therefore been investigated mainly by spectroscopic methods—IR, Raman, NMR, fluorescence, and atomic-absorption methods, X-ray electronic spectroscopy, etc. However, under these conditions one obtains at best information about the involvement of the O(6) atom of the oxopurine in the coordinate bond with platinum(II) but not about the mononuclear or polynuclear structure of the complexes. Measurements of the molecular weight are necessary for this purpose, which is hindered by the electrolytic character of the compounds and their poor solubility in non-polar solvents. Owing to the differential binding of *cis*-DDP by the DNA guanine, most of the studies have been devoted to the elucidation of the mode of binding of guanine, guanosine, and their derivatives in platinum(II) complexes.

Complexes whose composition corresponds to bidentate coordination have been isolated and investigated in a number of studies:[62] [PtdatGua]Cl_2, where dat = 3,4-diaminotoluene. The reaction of [PtdatCl$_2$] with guanosine was carried out in dimethylformamide (DMF), the complexes being isolated by adding the 1:1 acetone–ether mixture. Recrystallisation of the complex [PtdatGua]Cl_2 from a methanol–ether mixture leads to the formation of a complex of the triammine type with guanosine bound as a monodentate species, namely [PtdatGuaCl]Cl. The stretching vibration frequency $\nu(C{=}O) = 1645$ cm^{-1} in the complex [PtdatGua]$^{2+}$ is appreciably smaller than in the complex containing guanosine coordinated as a monodentate species, i.e. [PtdatGuaCl]$^+$ (1685 cm^{-1}) and in free guanosine; on this basis, the authors concluded that an unstable chelate of the N(7)–Pt–O(6) type is formed in the first compound. The change in the N(1)H chemical shift in the spectra of the complexes [in hexadeuteriated dimethyl sulphoxide (DMSO-d_6)] is also consistent with this hypothesis: the shifts are 10.82 p.p.m. for [PtdatGua]Cl_2 and 10.70 p.p.m. for [PtdatGuaCl]Cl; in the first complex, deshielding increases owing to the involvement of O(6) in coordination.

It has been demonstrated by X-ray electronic spectroscopy that in the solid complexes of *cis*-DDP with DNA which have been isolated the 1s[O(6)] ionisation energy of guanine is reduced by 0.5–0.7 eV, whereas no such decrease is observed in the binding of the *trans*-isomer.[63] The DDP and [PtenCl$_2$] complexes, which are capable of chelation, as well as their aquo-forms greatly reduce the intensity of the fluorescence in the DNA–ethidium bromide system.[64] It has been observed by the atomic absorption method that the absorption intensity in the complexes with the postulated chelate linkage, i.e. [Pt$(NH_3)_2$Gua]Cl_2 and [PtenGua]Cl_2, is smaller by a factor of two than in the complexes with the monodentate coordination of guanosine.[65] It has been established by potentiometric measurements that the reaction of DDP with DNA guanine is accompanied by the elimination of two chloride ions per molecule of the complex, while in the reaction with the *trans*-isomer one such ion is removed.[31] The conclusion that a platinum(II) chelate complex with guanine is formed via the N(7) and O(6) atoms was also reached on the basis of circular dichroism spectra.[66]

Complexes in which the bidentate coordination of the neutral guanosine molecule, namely [PtenGua]$(NO_3)_2$.$2H_2O$ and [PtenGua]$(ClO_4)_2$, synthesised by treating a solution of *cis*-[Pten$(H_2O)_2$]$^{2+}$ with guanosine in 1:1 proportions at 40 °C for 1 day, have been described.[67] The outer-sphere position of the NO_3^- and ClO_4^- ions follows from IR spectra [$\nu(NO_3^-) = 1380$ cm^{-1} and $\nu(ClO_4^-) = 1100$ cm^{-1}] and conductimetric data, which correspond to the decomposition of complexes of the type characteristic of 1:2 electrolytes. Comparative study of the IR spectra in the $\nu(C{=}O)$ region for complexes with monodentate and postulated bidentate coordination of guanosine showed that in the latter the $\nu(C{=}O)$ frequency is reduced by 20 cm^{-1}. When 1 equivalent of NaOH is added to aqueous solutions of the complexes, the pH increases from 4.5 to 7.2, but, as the reaction proceeds, it falls to 6.9. The addition of alcohol entails the formation of the compounds [Pten(Gua – H)]X.$2H_2O$, where X = ClO_4^- or NO_3^-, and [Pten(Gua – H)]I.$3H_2O$. As a result, the authors assume the possibility of the formation of a chelate especially for the anion (Gua – H)$^-$, but in concentrated solutions they do not rule out the possibility of the existence also of polymeric species with bridging anions.

The bidentate coordination of the anions of 6-oxopurines in platinum(II) complexes has been postulated.[38,67,68,69] Dilute solutions (10^{-4} M) of the complexes [Pten(Gua – H)]$(ClO_4)_2$.$2H_2O$, [Pten(Gua – H)Cl], and [PtenGua]$(NO_3)_2$ contain no polymers judging from circular dichroism spectra: the spectra of these complexes are analogous to those of free guanosine and its anion but differ from the spectra of [PtenGua$_2$].Cl_2, where the interaction of two neighbouring guanosine molecules leads to a two-phase signal.[67,70] The ^{195}Pt and ^{15}N NMR methods have been applied to solve the problem of the possible chelation of inosine in reactions with platinum(II) complexes.[71] The ^{195}Pt NMR spectra yield valuable information about the structure of the platinum complexes. The chemical shift of the ^{195}Pt nuclei changes appreciably as a function of the nature of the donor atoms in the coordination unit and the geometrical configuration of the complex. For example, the chemical shifts in the spectra of the isomeric aquo-complexes $[Pt(NH_3)_2(H_2O)_2]^{2+}$ differ by 209 p.p.m. The ^{195}Pt NMR spectra are usually recorded for specimens enriched in ^{15}N, since the ^{14}N nuclei, which possess a quadrupole moment, broaden the signals. The spin–spin coupling constant $^1J(^{195}Pt-{}^{15}N)$ is sensitive to the nature of the *trans*-ligand and can be used in its turn for the determination of the donor atoms and for the estimation of the *trans*-influence. The formation of polymeric hydroxo-complexes when solutions of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ are allowed to stand, can be followed clearly on the basis of the ^{195}Pt NMR spectra: the chemical shift in the specially prepared solutions is −1593 p.p.m. (using Na_2PtCl_6 as the external standard) and, when the solution is allowed to stand, new signals appear at −1161.8 p.p.m and −1520 p.p.m., referring respectively to $[Pt(NH_3)_2OH]_2^{2+}$ and $[Pt(NH_3)_2.OH]_3^{3+}$.[30,72–74]

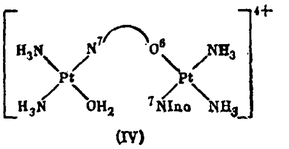
Signals of the initial complex [a triplet with $^1J(^{195}Pt-{}^{15}N) = 312$ Hz] and broad signals due to the formation of complexes of the triammine and tetrammine types with inosine were observed in the $\{^1H\}-{}^{195}Pt$ NMR spectra, with suppressed resonance of the protons, of the 1 : 1 mixture of *cis*-$[Pt(^{15}NH_3)_2Cl_2]$ and inosine, but signals corresponding to the $^{195}Pt-O(6)$ bond, which should have been present in the chelate, were not found.[71] However, the authors assume the formation of the N(7)–Pt–O(6) chelate in the 1 : 1 mixture of *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2]^{2+}$ with inosine, because the $\{^1H\}-{}^{15}N$ NMR spectrum of this system contains an additional signal displaced by 2 p.p.m. towards higher frequencies compared with the spectrum of the monoaquotriammine complex. The signal was absent from the spectrum of a solution of *cis*-$[Pt.(^{15}NH_3)_2(H_2O)_2]^{2+}$ containing adenosine 5′-monophosphate.

Chelation has been observed indirectly in the cobalt(II),[75] copper(II),[76] and nickel(II) [77] complexes of guanosine. Direct chelation has been demonstrated by X-ray diffraction in the copper(II) complexes of theophylline, which is a structural analogue of guanine.[78] It has been established by the same method that the DDP–*cis*-$Pt(NH_3)_2^{2+}$ fragment bound to DNA is located in the vicinity of the N(7) and O(6) atoms of guanine.[79] Quantum-chemical calculations agree with the occurrence of chelation.[80] Complexes of palladium with the chelated anions, namely $[Pd(Ino-H)_2]$ and $[Pd(Gua-H)_2]$, have been isolated.[81] The coordination of the guanosine anion via the deprotonated N(1) atom has been observed in the reaction of *cis*-$[Pt(DMSO)_2Cl_2]$ with inosine in an alkaline medium.[82]

Stereochemical relations more favourable for chelation obtain for 6-mercaptopurines, since the increase of the C–S bond length promotes the decrease of the strain on formation of the S(6)–N(7) chelate. Palladium(II) complexes with this type of bond have been observed.[83–85] Cationic, anionic, and non-electrolytic platinum(II) and palladium(II) complexes of 6-mercaptopurine bound as a bidentate species have been described.[86] The isomeric diamines $[Pt(NH_3)_2Cl_2]$ react differently with 6-mercaptopurine (6-mp): all the ligands are substituted in the *cis*-isomer and the complex $[Pt(6\text{-mp}-H)_2]$ is formed, while in the *trans*-isomer only two Cl^- ions are substituted, which is caused by the strong *trans*-influence of 6-mercaptopurine. The formation of the Pt–S and Pt–N bonds in the chelate has been confirmed by the EXAFS method.[87]

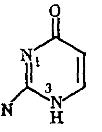
Experimental and theoretical studies, whose results conflict with the hypothesis of the formation of a direct chelate of the N(7)–O(6) type, have been carried out. Stereochemical objections have been raised by Sletten.[76] The interaction of the complexes $[Pten(H_2O)_2]^{2+}$ and $[PtenCl_2]$ with inosine and its derivatives at different pH has been investigated by the Raman spectroscopic and ^1H NMR methods.[53,54] For the ratio Ino/Pt ≤ 2, complexes with one or two inosine anions are formed in an alkaline medium. The H(8) and H(2) signals undergo an upfield displacement under these conditions. With increase of the Pt/Ino ratio from 1 to 4, the ^1H NMR spectra change qualitatively—the signals become broad, which has been attributed to the formation of polymeric species containing bridging inosine anions with participation of the N(1) and N(7) atoms.

In order to investigate the possible chelation reaction between *cis*-DDP and inosine and hypoxanthine, we investigated the complexes *cis*-$[PtA_2L](NO_3)_2$ (A = NH_3 or ½en and L = inosine or hypoxanthine), whose composition corresponds to bidentate binding, and the spectroscopic characteristics and acid properties of these compounds and the complexes of the triammine type $[PtA_2LCl]Cl$ with monodentate coordination of the ligands were compared. The complexes *cis*-$[PtA_2L](NO_3)_2$ were obtained by treating a solution of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with an equimolar amount of the ligand and were precipitated with acetone.[47] The acid titration curves for the complexes obtained differ sharply from the titration curves for the complexes with ligands bound as monodentate species: the acidity of the complexes *cis*-$[Pt.(NH_3)_2L](NO_3)_2$ is appreciably greater and the curves consist of a short initial section corresponding to the titration of a strong acid (0.20–0.25 equiv.of OH^- per mole) and a second section in the pH range 6–8. From the pH values in this section, one may conclude that it corresponds to the titration of a coordinated water molecule in the complex *cis*-$[PtA_2LH_2O]^{2+}$. Comparison of the titration curves for the complex *cis*-$[Pt(NH_3)_2Ino](NO_3)_2$ and the isomeric monoaquo-ions $[Pt(NH_3)_2InoH_2O]^{2+}$, prepared from the corresponding triammines by removing the Cl^- ion by treatment with $AgNO_3$, leads to the following conclusions: (1) the titration curves for *cis*- and *trans*-$[Pt(NH_3)_2InoH_2O]^{2+}$ differ little from one another; this conflicts with the hypothesis of the existence of the N(7)–Pt–O(6) chelate in solutions, since the capacity for chelation is characteristic only of the *cis*-isomer, which would have led to a difference between the titration curves; (2) the titration curves for the isomeric monoaquo-cations and *cis*-$[Pt(NH_3)_2Ino](NO_3)_2$ are also similar. Hence one may conclude that solutions of these compounds contain species with analogous compositions and structures. These can be (1) the monomeric aquo-cations *cis*-$[Pt(NH_3)_2InoH_2O]^{2+}$ and (2) the dimeric and polymeric cations linked by bridging inosine molecules via the N(7) and O(6) atoms in which the acid dissociation of N(1)H is enhanced. The contents of these species can be estimated from the relative sizes of the corresponding sections of the titration curves: 75% of platinum exists as the monoaquo-cation and 25% as the dimer. The participation of the O(6) atom in the coordinate bond follows from the ^{13}C NMR spectra of the complex $[Pt(NH_3)_2.Ino](NO_3)_2$ in D_2O: (1) the C(5) and C(8) signals of inosine in the complex undergo the greatest downfield shift, which indicates the presence of the Pt–N(7) bond; (2) the C(2) signal changes little under these conditions, i.e. there is no Pt–N(1) bond; (3) the form of the C(6) signal differs sharply from that of the signal in the spectra of complexes with monodentate coordination of inosine—it has a multiplet structure, is appreciably broadened, and has been displaced downfield. Comparison of the X-ray emission spectra of the complexes *cis*-$[Pt(NH_3)_2Hyp]\{B(C_6H_5)_4\}_2$ and *cis*-$[Pt(NH_3)_2.(Hyp)_2]\{B(C_6H_5)_4\}_2$ indicates a decrease of electron density at the O(6) atom in the first compound, which agrees with the involvement of the atom in the coordinate bond. The circular dichroism spectra of these compounds are of the single-phase character (like the spectra of free inosine and the complexes having the *trans*-configuration), in contrast to *cis*-$[Pt(NH_3)_2Ino_2]Cl_2$, where there is a possibility of band splitting owing to the π-interaction of inosine molecules in close proximity. This set of data has led us to the conclusion that formula (IV) may be attributed to the cationic complex.



(IV)

A paper published a year and a half after our communication[88] also described the application of the method involving the acid titration of the isomers $[Pt(NH_3)_2(9\text{-}C_2H_5Gu)H_2O]^{2+}$ in order to detect chelation. On the basis of the similarity of the titration curves for the isomers, it was concluded that there are no chelates with a N(7)–Pt–O(6) bond. The consumption of alkali in the titration after the jump at pH 8 was in our case 1 equiv. per mole of platinum; a strongly acidic section, corresponding to the consumption of 0.25 equiv. of OH^- per mole, was also observed. The character of the titration curve was likewise explained by the acid dissociation of H_2O in *cis*-$[Pt(NH_3)_2(9\text{-}C_2H_5Gu)H_2O]^{2+}$ and a dimer containing bridging and terminal 9-ethylguanine molecules. It has been suggested that the bridge bonds are formed via the N(7) and N(1) atoms of 9-ethylguanine and that the strong acid properties are due to the dissociation of N(3)H in an unusual tautomeric form of 9-ethylguanine. We believe that the involvement of the N(1) atom in the bridge bond is less probable than the involvement of the O(6) atom. In the analogous complexes of inosine, the presence of the Pt–O(6) bond has been confirmed by a number of methods; furthermore, the unusual tautomeric form of 9-ethylguanine with a proton at N(3) corresponds to one of the tautomeric forms of isocytosine:



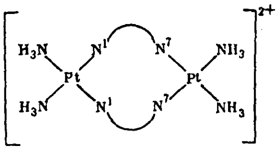
(V)

However, isocytosine has weak acid properties ($K_a = 3.2 \times 10^{-10}$) and K_a for the complex *cis*-$[Pt(NH_3)_2(\text{iso-Cyt})Cl]Cl$ which we synthesised is 1.3×10^{-7}. The strong acidity along the first section of the titration curve is therefore hardly likely to be associated with the formation of such a tautomer.

A combination of the most modern research techniques has been used by Raudashl-Siever et al.[89], namely high-performance liquid chromatography (HPLQ) and ^{195}Pt NMR, for the investigation of the nature of the products formed in the reaction of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with guanine and its methyl-substituted derivative for different ratios and concentrations of the components, different pH (2 and 7), and different contact times (temperature 60 °C). The HPLQ method makes it possible to detect the formation of a number of compounds in solution. The predominant complexes were isolated on the preparative scale and analysed. They include dinuclear complexes with one or two bridging guanine anions—$[Pt_2(NH_3)_4(Gu-H)](NO_3)_3.2H_2O$ and $[Pt_2(NH_3)_4.(Gu-H)_2](NO_3)_2.2H_2O$—and the monomeric complex $[Pt(NH_3)_2(Gu-H)Gu]NO_3$. The formation of complexes with chelated molecules or anions of guanine has not been observed.

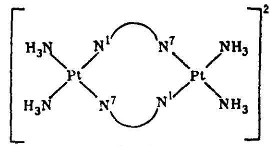
(c) Bridge Type Coordination of Purines and their Nucleosides

Complexes of this type include the dinuclear complexes with bridging guanine anions. The complex $[Pt_2(NH_3)_4(Gu-H)_2].(NO_3)_2.2H_2O$ contains the coordination unit PtN_4 according to ^{195}Pt NMR spectra; two ^{195}Pt signals (−2416 and −2468 p.p.m.) indicate the presence of two isomers:



(VI)

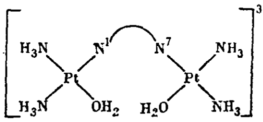
and



(VII)

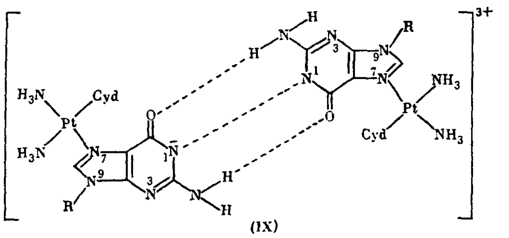
"head to head" "head to tail"

The ^{195}Pt NMR spectra of the dimer $[Pt_2(NH_3)_4(Gu-H)].(NO_3)_3.2H_2O$ contains one signal at −1015 p.p.m., which corresponds to the PtN_3O unit and the coordination formula



(VIII)

In both compounds the bridge is formed via the N(1) and N(7) atoms of the guanine anion. We explain the acid properties of the complexes $[PtA_2L](NO_3)_2$ (A = NH_3 or ½Eu; L = Ino or Gua) by the formation of dimers with an inosine and guanosine bridge bond via the N(7) and O(6) atoms.[47,90] This type of bonding had been postulated earlier in the polymeric platinum(II) and palladium(II) complexes with these ligands.[91,92] The bridge bond via the N(3) and N(9) atoms becomes possible for guanine derivatives dimethylated at N(1) and N(7).[89] The binding of two platinum(II) atoms by the neutral hypoxanthine molecule via N(3) and N(9) has been established in the complex $[Pt_2Gly_2Cl_4Hyp]$, where Gly = glycine, formed in the reaction of $K_2[PtGly_2Cl_2]$ with hypoxanthine, in view of the identical shifts of the H(2) and H(8) signals on coordination.[93] Yet another type of binding, via three hydrogen bonds between guanine and its anion, has been indicated in the dimeric complex $[Pt_2(NH_3)_4.Cyd_2Gu(Gu-H)]^{3+}$, where Cyd = cytidine:[94]

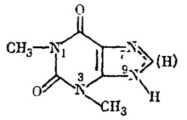


(IX)

In conclusion of this Section, one may say that the presence of the N(7)–Pt–O(6) chelate in the complexes with the ratio L/Pt = 1, where L = 6-oxopurines or their nucleosides, does not follow self-evidently from spectroscopic and physicochemical studies of these compounds and has not been confirmed by X-ray diffraction. The existence of these compounds, especially in solutions, as mixtures of mononuclear monoaquo-complexes and dimeric or polymeric species containing bridging nucleoside ligands with participation of the O(6) atom in the bridge bonds appears more likely. The ratios of these forms depend on the concentration and pH of the solution: in an alkaline medium, the probability of the formation of polymeric structures with bridging anions increases and one cannot rule out the existence of chelates with the anion. Investigation of the structures of these compounds by X-ray diffraction and the determination of their molecular weight in solution are undoubtedly required.

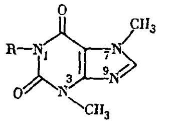
2. Platinum(II) Complexes of 2,6-Dioxopurines

The platinum(II) and platinum(IV) complexes of methylated 2,6-dioxopurines have been investigated:



(X)

N-1,3-dimethylxanthine, theophylline (Thp)



(XI)

R = H: *N*-3,7-dimethylxanthine, theobromine (TeO); R = CH_3: *N*-1,3,7-trimethylxanthine, caffeine (Caf)

Tautomerism is possible for theophylline [the proton is located at the N(7) or N(9) atom]. These ligands are biologically active. Caffeine enhances the antitumour activity of DDP.[95] The ligands contain various nitrogen atoms in the heterocycle blocked by methyl groups, which makes it possible to investigate the bond between the metal and a definite nitrogen atom. By treating a solution of $K_2[PtCl_4]$ in 0.5 *N* HCl with theophylline, it was possible to isolate complexes having the composition $(ThpH)_2[PtCl_4]$ and $(ThpH)[PtThp.Cl_3]$, the former with an outer theophyllinium cation and the latter with an outer cation and coordinated theophylline molecule linked by a bond via the N(9) atom.[96,97] The theophylline anion is coordinated to platinum(IV):[98] the reaction of $[Pt(CH_3)_3(H_2O)_3]^+$ with sodium theophyllinate leads to the formation of the complex $[Pt(CH_3)_3(Thp-H)]$, containing the anion (Thp - H) and the Pt(IV)–N(7) bond. The compound is monomeric in solutions in DMSO and C_2H_5OH. The molecular weight of the complex in $CHCl_3$ and CH_2Cl_2 corresponds to the trimer. On the basis of the $^1H-^{195}Pt$ and $^{13}C-^{195}Pt$ spin–spin coupling constants, it has been established that the theophylline anion plays the role of a tridentate ligand, forming a chelate bond via the N(7) and O(6) atoms with platinum(II) and a bridge bond via N(9) with another platinum(II) atom.

The caffeine complex $(PPh_3CH_3)[PtCafCl_3]$, where $(PPh_3.CH_3)^+$ is the triphenylmethylphosphonium cation, has been isolated and its structure investigated; the bond between caffeine and platinum(II) is formed via the N(9) atom.[99] The anionic complex $K[PtCafCl_3]$ was found to possess antitumour activity: towards lymphocytoleukaemia P-388, the inhibition coefficient was 150%. Mixed non-electrolytes having the composition $(MCafLCl_2)$ [M = Pt(II) or Pd(II); L = Ado, Ino, or Gua] were isolated following the interaction of equimolar amounts of nucleosides and $K[PtCafCl_3]$ in an aqueous DMSO solution.[100] The coordination of caffeine via the N(9) atom and of nucleosides via the N(7) atom has been established by the ^1H and ^{13}C NMR methods. The *cis*-structure of the non-electrolyte follows from the presence of two absorption bands in the Pt–Cl region. Treatment of the complexes with alkaline solutions leads to the isolation of complexes with nucleoside anions: [MCaf.(Ino - H)Cl] and [MCaf(Gua - H)Cl]. The decrease of $\nu(C{=}O)$ in the spectra of the inosine and guanosine anions compared with the free ligand has been interpreted by the authors as a result of the formation of a Pt–O(6) bond, either of the N(7)–Pt–O(6) chelate type or the bridge type.

The product $[Pt(Caf-H)Cl]_2$, isolated in small amounts in the reaction of $K_2[PtCl_4]$ with caffeine (1:1) in 0.5 *N* HCl at 50 °C, is extremely unusual.[100] Its dimeric structure has been confirmed by measurement of its molecular weight. The far IR spectrum shows a $\nu(Pt-Cl)$ band at 305 cm^{-1}, corresponding to the Pt–Cl–Pt bridge bond. The signal of the H(8) proton is absent from the ^1H NMR spectrum of the complex, which has been explained by the formation of the Pt–C(8) σ-bond. However, the proposed structure requires further confirmation, since the presence of the Pt–C(8) σ-bond has not been demonstrated directly by the ^{13}C NMR method and the heterolytic cleavage of the C(8)–H bond in an acid medium is unlikely. It is also noteworthy that not one complex with the caffeine anion has been described hitherto.

A σ-bond of the ylide, carbene type is formed between Ru(III) and the caffeine C(8) atom in the reaction with $[Ru(NH_3)_3(H_2O)_3]^{3+}$.[101] The complex $[Ru(NH_3)_3Cl_2Caf]Cl.H_2O$ with a neutral caffeine molecule, in which the presence of the Ru(III)–C(8) bond has been established by X-ray diffraction, has been isolated. The Ru–C(8) distance (2.03 Å) corresponds to a strong, short bond. Complexes with this type of bond, namely $[Ru(NH_3)_4CafCl]Cl_2.2H_2O$ and $[Ru(NH_3)_4TeoCl]Cl_2.2H_2O$, have been described.[102] In both complexes the Ru(III)–N(9) bond is sterically hindered by the $N(7)CH_3$ group. Theophylline, in which the group is absent, is capable of binding both via the N(7) atom and the O(6) atom.

As a consequence of acid dissociation at N(7) and N(1)H, theophylline and theobromine are able to form complexes with coordinated anions, both Ru(III)–N(9) and Ru(III)–C(8) bonds being formed in the case of theophylline. A bond of the M–C(8) type is also present in the complexes of $HgCH_3^+$ with xanthine.[103]

Non-electrolytes having the composition $[PtThp_2Cl_2].2H_2O$ and $[PtCaf_2Cl]$ have been obtained in the reactions of $K_2[PtCl_4]$.[104] The isomeric triammines $[Pt(NH_3)_2LCl]Cl$ and the *cis*-tetrammines $[Pt(NH_3)_2(Thp)_2](NO_3)_2$ have been isolated after reactions involving *cis*- and *trans*-$[Pt(NH_3)_2.Cl_2]$. According to ^{13}C NMR data, the greatest downfield shift relative to the proton-donating ligands is observed on coordination for the signals due to the C(4) and C(8) atoms (4–7 p.p.m.), which indicates the presence of the Pt–N(9) bond. In the spectra of isomeric complexes having two theophylline molecules, two sets of ^{13}C signals are observed: one corresponding to coordination via the N(9) atom and the other, with an appreciable shift of the C(5) signal, which justifies the conclusion that the bond linking the second theophylline molecule is formed via the N(7) atom. The signals of the H(8) proton and of the methyl groups are also doubled in these compounds, which agrees with the hypothesis that the theophylline molecules are bound via both the N(9) and N(7) atoms.

3. Platinum(II) Complexes of Adenine and Adenosine

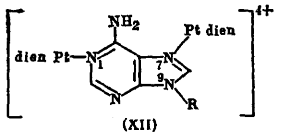
Adenine and its nucleoside adenosine (III) are 6-aminopurines. Adenine and adenosine possess weak basic properties, owing to the possibility of protonation at the N(1) atom: $pK_a[N(1)H^+] = 4.1$ (Ad) and 3.6 (Ado). The N(9)H group in adenine is capable of weak acid dissociation: $pK_a = 9.8$.[49] The following main types of coordinate bonds can be postulated for these ligands: (1) a monodentate bond via the N(1) or N(7) atoms; (2) a bridge bond in which the adenosine molecule binds two platinum atoms via the N(1) and N(7) atoms; (3) a bidentate bond via the N(1) [or N(7)] atom and the NH_2 group.

The monodentate coordination of adenine and adenosine via the NH_2 group is probable owing to the p,π-conjugation of the unshared electron pair of the NH_2 group with the ring.

The involvement in the bonds of the atom N(3), which is blocked by the D-ribose residue in close proximity, is just as unlikely. In addition to these types of bonding, adenine is capable of being coordinated in the form of an anion as a result of the acid dissociation of the HN(9) groups.

The principal conclusions about the interaction of adenine and adenosine with platinum(II) complexes have been reached by Theophanides and co-workers.[37,105] The non-electrolytic complexes $[PtL_2X_2]$ ($X = Cl^-$ or Br^-) were isolated after treating a solution of $K_2[PtCl_4]$ with adenine, adenosine, and tri- and tetra-acetyladenosine. The signal of the H(8) proton undergoes the greatest downfield shift in the ^1H NMR spectra of the complexes: $\Delta\delta_{H(8)} = 0.92$ p.p.m. and $\Delta\delta_{H(2)} = 0.21$ p.p.m.; this indicates the coordination of the ligand via the N(7) atom. The monodentate coordination of adenosine was observed also by Ettore.[106] Adenosine and 9-methyladenine protonated at N(1) are also capable of such coordination: the complexes $[Pt(AdoH)Cl_3]$ and $[Pt(9\text{-}CH_3.$ $.AdH)Cl_3]$ are formed in 3 *N* HCl.[107] Other adenosine complexes containing the Pt–N(7) bond have also been isolated: the isomeric $[Pt(NH_3)_2Ado_2]Cl_2$ [108] and $[PtAdo_4]Cl_2$.[109] At the same time, for adenine there is much more evidence than for oxopurines and their nucleosides indicating the involvement of the N(1) atom in the monodentate bond with platinum(II). The coordination of adenosine via the N(7) atoms is promoted by an acid medium. It has been shown in relation to the reaction of $[PtdienH_2O]^{2+}$ with adenosine that in a neutral medium there is also a possibility of the formation of complexes with a Pt–N(1) bond.[37,110] The complexity of the ^1H NMR spectrum of the complex $[Pt(TAA)_2Cl_2]$ (TAA = triacetyladenosine), which has four signals instead of two for H(2) and H(8), was explained by the formation of complexes with three bond types:[105] N(7)–Pt–N(7), N(1)–Pt–N(1), and N(7)–Pt–N(1). The same three types of monodentate binding of adenosine were observed in the reactions of $[Pt(NH_3)_3Cl]Cl$ with adenosine with the ratio Ado/Pt = 2.[111] The products were separated by high performance liquid chromatography and their structure was demonstrated by spectrophotometric measurements at different pH. The double binding via the N(1) and N(7) atoms was observed also in the platinum(II) complexes of 9-methyladenine.[112]

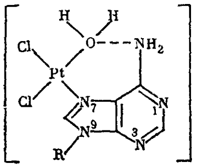
The formation of dinuclear complexes with a bridge type coordination of adenosine was first observed in solutions by the isomolar series (continuous variations) spectrophotometric method.[113] An analogous result was obtained in the study of the ^1H NMR spectra of solutions of [PtdienCl]Cl containing adenosine and an excess of the platinum(II) complexes, i.e. for a ratio Pt/L > 2.[37] Under these conditions, approximately equal downfield shifts of the signals of the H(2) and H(8) protons, amounting to 0.9–1 p.p.m., are observed. Both signals acquire the triplet form as a result of the spin–spin interaction with the ^{195}Pt nucleus [with the constant $^3J_{^{195}Pt^1-{}^1H(2,8)} = 26$ Hz]. The authors believe that the dinuclear complexes (XII) with a bridge type coordination of adenosine are formed in solution:



(XII)

The presence in solutions of complexes containing the Pt–N(1)–N(7)–Pt linkage as a result of the reactions of $[PtacacCl_2]^-$ (acac = acetylacetone) and *cis*-$[PtDMSOCl_3]^-$ with adenosine has been demonstrated by ^1H NMR.[114] Isomeric *cis*- and *trans*-complexes with a similar bond have been isolated in a pure state: $[Pt(NH_3)_2ClAdoPt(NH_3)_2Cl]Cl_2$ and $[Pt(NH_3)_2ClAdPt(NH_3)_2Cl]Cl_2$.[115,116] Anionic dinuclear complexes $K_2[PtCl_3AdoPtCl_3]$ with bridging adenosine molecules have also been described.[39] The tendency of adenine and adenosine molecules towards the bridge type of binding is manifested by the formation of polymeric complexes. Polynuclear complexes with 9-methyladenine having the composition $[Pt(9\text{-}CH_3Ad)Cl_2]$ have been described.[105] The formation of a series of polymeric complexes in the reaction of $K_2[PtCl_4]$ with adenine has been indicated.[117] A trinuclear complex with adenine anions $(Ad-H)^-$ having the composition $[Pt_2Ad(Ad-H)_2C_2H_5OH][PtI_4]$ has been isolated.[118]

The bidentate binding of adenine and adenosine to platinum(II) presupposes the involvement in the coordination of the NH_2 group and one of the nitrogen heteroatoms—N(1) or N(7) (most probably). The hypothesis of the bidentate binding of these ligands has been put forward on the basis of spectrophotometric measurements.[13,113] Complexes whose composition corresponds to this coordination have been isolated: $[PtAdX_2].2H_2O$ ($X = Cl^-$ or Br^-) and $[PtAdoI_2]$. $.2H_2O$.[119] A strong downfield shift of the signal of the NH_2 group is observed in the ^1H NMR spectra of these compounds in DMSO-d_6, which is regarded as evidence for its involvement in binding. The complexes $[PtAdoCl_2]$, $[PtAdCl_2H_2O]$, and $[PtAdCl_2]$ have been isolated.[120] The complex [PtAdo. $.Cl_2]$ is anhydrous and monomeric and frequencies characteristic of Pt–Cl–Pt bridge bonds are absent from its IR spectrum; according to far IR spectroscopic data, it has the *cis*-configuration. A chelate structure involving the NH_2 group and the N(7) atom has been proposed for this complex. The formation of a chelate in which the NH_2 group of the adenine molecule is bound by a hydrogen bond to the oxygen atom of a water molecule is more probable for the hydrated complex:



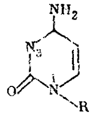
(XIII)

The insoluble complex $[PtAdCl_2]$ is apparently polymeric. Solutions of the non-electrolytic complexes $[PtAdCl_2H_2O]$ and $[PtAdoCl_2]$ in DMSO exhibit an inhibiting effect amounting to 50–60% on four strains of tumours[121] and at the same time they are less toxic than *cis*-DDP. The cationic complexes *cis*-$[Pt(NH_3)_2Ado](NO_3)_2$, in which the formation of a chelate involving N(7) and the NH_2 group can also be postulated, have been described.[115,116] The complexes differ from compounds with monodentate coordination of adenosine in their ^1H NMR spectra and acid properties. However, a final conclusion about the structure can be reached on the basis of X-ray diffraction analysis, which so far has not been possible owing to the lack of crystals suitable for this purpose.

III. THE SYNTHESIS, STRUCTURE, AND PROPERTIES OF PLATINUM(II) COMPLEXES OF PYRIMIDINE BASES AND THEIR NUCLEOSIDES

1. Complexes of Cytosine and Its Derivatives

Cytosine [Cyt, (XIV), R = H] together with guanine belong to the class of DNA bases which react preferentially with platinum complexes. In terms of their ability to interact with DDP, cytosine is in the second place after guanine and among pyrimidine bases it is in the first place. The keto-amino-form is most characteristic of cytosine and its nucleoside cytidine [Cyd, (XIV), R = β-D-ribosofuranosyl]:[122]



(XIV)

Cytosine and cytidine are ambident ligands, since they contain several potential donor atoms. They can be the heterocyclic N(3) and N(1) atoms, the exocyclic NH_2 group, and the exocyclic oxygen atom.

The binding of cytosine and its derivatives via the exocyclic amino-group is unlikely for the same reason as in the case of adenosine. The binding of metal ions via the amino-group becomes possible after its deprotonation. In the free ligands, the acid properties of the NH_2 group are extremely weak ($pK_a = 16$),[125] but coordination enhances them. The ribose residue of cytidine is not involved in the coordinate bond.

The principal site of the coordination of cytosine and cytidine to metal ions is one of the heterocyclic nitrogen atoms. In order to determine which particular atom, it is useful to compare the capacities of these atoms for protonation. It follows from spectroscopic (IR and ^1H NMR) and X-ray diffraction studies and also calculations of electron density that cytosine and cytidine are protonated in the N(3) position.[124–126] The pK_a are 4.6 for Cyt $N(3)H^+$ and 4.2 for Cyd $N(3)H^+$.[127] On this basis, one can postulate that cytosine and cytidine are also coordinated in the platinum(II) sphere via the N(3) atom. The formation of complexes of cytosine and its derivatives with platinum(II) has been investigated in most cases in solutions with the aid of ^1H NMR. Studies in which individual complexes with these ligands were isolated and their structure demonstrated are less common in the literature.

In one of the first investigations[13] by differential spectrophotometry at different pH, a study was made of the interaction of cytidine with the geometrical isomers of $[Pt(NH_3)_2 . Cl_2]$ at 37 °C. Analysis of the absorption spectra of the equilibrium mixture led the authors to the conclusion that a chelate is formed with participation of N(3) and the $4\text{-}NH_2$ group in the reaction with the *cis*-isomer and that there is monodentate binding via the N(3) atom in the reaction with the *trans*-isomer. However, further studies failed to confirm the formation of the chelate.

Studies have been made[37,128] of the ^1H NMR spectra of solutions of the platinum(II) complexes of cytosine and cytidine. Two doublet signals of the H(6) (7.35 p.p.m.) and H(5) (5.60 p.p.m.) protons and also a broad signal of the NH_2 group at 7.1 p.p.m. were observed in the ^1H NMR spectrum of free cytosine in DMSO-d_6.[129] The spin–spin coupling constant $^3J_{H(5)-H(6)} = 7$ Hz. On formation of the cytidine complex in the reaction with [PtdienCl]Cl, the signal of the H(5) proton undergoes a downfield shift of 0.13 p.p.m., which is somewhat greater than the shift of the H(6) proton (0.11 p.p.m.). Spin–spin interaction with the ^{195}Pt nucleus has been observed for the H(5) atom: instead of a doublet, two triplets with the intensity ratios 1:4:1 were produced. The spin–spin coupling constant is $^4J_{^{195}Pt-^1H(5)} = 8$ Hz, which is close to the value observed for the *meta*-proton in the platinum(II) complexes of pyridine.[130] The splitting of the signal of the H(6) proton by the ^{195}Pt nucleus was not observed. These data led the authors to the conclusion that cytidine is coordinated via the N(3) atom. A similar bond is formed also in the coordination of the 5-mononucleotide of cytidine (cytidine 5′-monophosphate or 5′-CMP).[128]

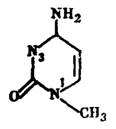
The ^1H and ^{13}C NMR spectra of the complexes of $PtCl_2 . 2DMSO$ and $PdCl_2 . 2DMSO$ with cytosine and cytidine in solutions in DMSO-d_6 have been thoroughly investigated.[129] In these systems too, $\Delta\delta[H(5)] = 0.18$ p.p.m. $> \Delta\delta[H(6)] = 0.11$ p.p.m. In the solutions of cytosine in DMSO-d_6, the signal of the proton in the NH_2 group is at 6.91 p.p.m. and is remote from the signal of N(1)H (10.27 p.p.m.). Coordination leads to a downfield shift of the signal of the NH_2 proton and to its splitting into two components: 8.59 and 8.25 p.p.m., because the rotation about the C–N bond in the complex is hindered. In the ^{13}C NMR spectra, the greatest shift has been observed for the C(2) and C(4) signals, both undergoing an upfield shift: $\Delta\delta[C(4)] = 1.3$ Hz and $\Delta\delta[C(2)] = 3.1$ Hz (WH90 Bruker spectrometer with a field strength of 21.14 kG under pulsed Fourier conditions). Coordination influences also the spin–spin coupling constant $^1J_{^{13}C-^1H}$, which changes to a greater extent for the carbon atoms located nearer the coordination centre: $\Delta\,^1J_{^{13}C(5)-^1H(5)} = 10$ Hz $> \Delta\,^1J_{^{13}C(6)-^1H(6)} = 3$ Hz. Thus the results of our study demonstrate convincingly the involvement of the N(3) atom in coordination. The complexity of the spectra due to the fact that the reaction does not go to completion (~80%) and because the solution contains the free ligand is one of the methodological disadvantages of the above study. The authors were also unable to observe the $^{195}Pt-^1H$ spin–spin interaction. It has been stated[131] that one of the causes hindering the manifestation of the spin–spin splitting may be the anisotropy of the relaxation of the chemical shifts arising in recording at high frequencies (~100 MHz).

The formation of chelates of the type $N(3)-Pt-NH_2$ in reactions with platinum(II) complexes is not characteristic of cytosine and cytidine. A similar relationship has been proposed for $[Pt\,Cyt\,I_2]$ complexes,[119] but without a convincing proof.

Cytosine- and cytidine-containing platinum(II) complexes of the triammine type, namely *cis*-$[PtA_2LX]X$ (A = NH_3 or ½en), are of great interest. These compounds can be formed in the first stage of the reaction of DDP and $[PtenCl_2]$ with the pyrimidine bases in DNA. The triammines *cis*-$[PtA_2LX]X$ (L = Cyt or Cyd; A = NH_3 or ½en; X = Cl^-, Br^-, or NO_2^-) have been synthesised.[132,133] The complexes have been obtained on heating *cis*-$[PtA_2X_2]$ with an equimolar amount of the ligand, evaporation, and precipitation with acetone. Their structure was demonstrated by measuring the electrical conductivity (100–120 Ω^{-1} cm^2 mol^{-1}) and by the presence of the $\nu(Pt-X)$ absorption band in the long-wavelength absorption spectra. The ^1H NMR spectra of the triammines in D_2O and DMSO-d_6 indicate the coordination of cytosine and cytidine via the N(3) atom: for all the compounds, $\Delta\delta[H(5)] > \Delta\delta[H(6)]$. This conclusion also follows from the ^{13}C NMR spectra: the greatest shift in coordination has been observed for the C(2) and C(4) carbon atoms, which are in neighbouring positions relative to N(3): $\Delta\delta[C(2)] = 8.9$ p.p.m. and $\Delta\delta[C(4)] = 5.6$ p.p.m. in the spectrum of *cis*-$[Pt(NH_3)_2 . CytCl]Cl$, while the chemical shifts for the C(5) and C(6) atoms differ by 0.7 and 1.5 p.p.m. respectively. Coordination in the platinum(II) sphere greatly enhances the acid properties of cytosine as a result of the dissociation of N(1)H: $K_a = 6.1 \times 10^{-13}$ for cytosine[127] and $K_a = 5.0 \times 10^{-10}$ for *cis*-$[Pt(NH_3)_2CytCl]Cl$. The replacement of Cl^- by Br^- and NO_2^- leads to some decrease of acidity, apparently a result of the enhancement of the σ-donor properties of the acido-ligands. The hydrolytic stability of the bond in the complex *cis*-$[Pt(NH_3)_2CytCl]Cl$ has also been characterised: $K_{inst} = (4.0 \pm 0.5) \times 10^{-4}$.[134]

The communications examined contain the results of the investigation of the reactions of cytosine and cytidine with platinum(II) complexes having two or one chloride ions. The interaction of these ligands with $K_2[PtCl_4]$ is much more complex. In this case the nucleophilic substitution of the chloride ions is accompanied by the formation of polymeric products—the so-called "platinum pyrimidine blues".[135] The "blues" are obtained in an alkaline medium; their formation is apparently associated with the deprotonation of the ligands. A solid diamagnetic amorphous blue product having the composition $K_{0.2}PtCydCl_{1.5}(OH)_x(OH_2)_y$ has been isolated. On the basis of the ^1H NMR spectra and reactions with reductants ($NaBH_4$), the authors assume that the "blue" contains partially oxidised platinum and the cytosine anion, formed as a result of the deprotonation of the amino-group, is bound to platinum(II) by means of a chelate or bridge type bond via this group and the N(3) atom.

Among cytosine derivatives, the formation of platinum(II) complexes with methylcytosine (XV) ($1\text{-}CH_3Cyt$) has been studied to the greatest extent.

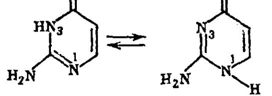


(XV)

Cationic complexes with the *cis*-structure have been isolated—the tetrammines $[Pt(NH_3)_2]$ $(1\text{-}CH_3Cyt)_2(NO_3)_2.$ $.1\text{-}CH_3Cyt$ [136,137] and the triammines *cis*-$[Pt(NH_3)_2(1\text{-}CH_3.$ $.Cyt)Cl]X$ ($X = Cl^-$ or NO_3^-).[138] It was established by ^1H NMR, on the basis of the greater shift of the signal of the H(5) proton than the shift of the H(6) proton signal on coordination and the triplet splitting of the H(5) proton signal, that the coordination is via the N(3) atom; it was confirmed for the tetrammine by X-ray diffraction. The triammines are unstable both in aqueous solution and on heating. In the latter case NH_2 is split off and *trans*-$[PtNH_3Cl_2(1\text{-}CH_3Cyt)]$ is formed.[139] A tetrammine with three molecules of 1-methylcytosine, namely $[Pt(NH_3).$ $.(1\text{-}CH_3Cyt)_3](ClO_4)_2$, was isolated after starting with the *trans*-non-electrolyte $[PtNH_3Cl_2(1\text{-}CH_3Cyt)]$.[140] The authors regard the formation of this compound as evidence for yet another pathway leading to the interaction between the DDP and DNA bases, namely one involving the displacement of NH_3 and the binding of three DNA bases. However, the elimination of NH_3 from *cis*-DDP under conditions simulating cytoplasm has not been demonstrated experimentally and there are no data indicating the presence of antitumour activity in the mixed *trans*-non-electrolyte $[PtNH_3ACl_2]$.

Among the platinum(II) complexes containing the neutral 1-methylcytosine molecule, there are also rarely encountered monomeric complexes with the terminal ligands OH^- and H_2O, namely $[Pt(NH_3)_2(1\text{-}CH_3Cyt)OH]NO_3.2H_2O$ and $[Pt(NH_3)_2.$ $.(1\text{-}CH_3Cyt)H_2O](NO_3)_2.H_2O$.[141] In contrast to cytosine, 1-methylcytosine is capable of being coordinated in the form of an anion via a bridge-type bond involving the N(3) atom and the deprotonated NH_2 group. It has been demonstrated by X-ray diffraction that such a bond occurs in the complex $[Pt(NH_3)_2(1\text{-}CH_3Cyt)_2Pt(NH_3)_2](NO_3)_2$.[142] The complex was isolated after treating the dimer $[Pt(NH_3)_2OH]_2(NO_3)_2$ with 1-methylcytosine in proportions of 2 : 1. In the same communication it is stated that there is a possibility of obtaining complexes in which platinum has the formal oxidation state of 2.5+: the complex $(H_2O_2)[Pt(NH_3)_2NO_2(1\text{-}CH_3.$ $.Cyt\text{-}H)_2Pt(NH_3)_2NO_2](NO_3)_2$, with an octahedral environment around the platinum atoms, has been obtained in small amounts—yield 2%. Structural data confirm the presence of the Pt–Pt bond for atoms in an oxidation state higher than 2+; thus the Pt–Pt distance in this complex is 2.584 Å, while in the platinum(II) and platinum(III) dimers these distances are respectively 2.970 Å and 2.466 Å.[143,144] In our view, the properties of this compound and the conditions governing its formation require further study, since there has been no full analysis of the complex, its yield is very low, and finally the formation of the $H_5O_2^+$ cation at pH 6 is unlikely.

The complexes (III) of platinum(II) with isocytosine (iso-Cyt), a cytosine isomer, have been described:[133,145]



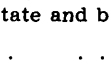
(a) (b)

(XVI)

Isocytosine exists mainly in the form of two tautomeric forms (a) and (b).[146] Complexes of this ligand of the triammine and tetrammine types having the *cis*-structure have been isolated: $[PtA_2(iso\text{-}Cyt)Cl]Cl$ and $[PtA_2(iso\text{-}Cyt)_2]Cl_2$ ($A = NH_2$ or $\frac{1}{2}en$).[145] Coordination is accompanied by a hypsochromic shift of the ring vibrations and a large downfield shift of the signal of the H(5) proton in the ^1H NMR spectra of the complexes in DMSO-d_6, which suggests the formation of a coordinate bond via the N(3) atom of the tautomeric form (XVIb). Isocytosine is characterised by much more pronounced acid properties than cytosine: $K_a = 3.2 \times 10^{-10}$.[127] The same also applies to platinum(II) complexes of isocytosine: $K_a = 5.0 \times 10^{-10}$ for *cis*-$[Pt(NH_3)_2.$ $.LCl]Cl$ ($L = Cyt$) and 1.3×10^{-7} for the same complex with $L = iso\text{-}Cyt$; $K_a^1 = 4.3 \times 10^{-10}$ for *cis*-$[Pt(NH_3)_2L_2]Cl_2$ when $L = Cyt$ and 3.2×10^{-7} when $L = iso\text{-}Cyt$.[133,145]

2. Platinum(II) Complexes of Aminopyrimidines

Apart from the formation of platinum(II) complexes of natural aminopyrimidines (cytosine and cytidine), studies have also been made of the formation of complexes with other aminopyridimidines. The platinum(II) complexes of 2-aminopyrimidine (2-Apm) and its substituted derivatives (XVII) have been most thoroughly investigated:[116,147–150]



(XVII)

where $R = H$, CH_3, OCH_3, or C_6H_5.

The presence of several potential donor atoms and groups in aminopyrimidine molecules suggests different types of binding of these ligands to platinum(II). Two main types of coordination—monodentate and bridge type—have been established.

In the reactions of 2-aminopyrimidine with $K_2[PtX_4]$ ($X = Cl^-$, Br^-, or I^-), non-electrolytic complexes with ligands involved in monodentate coordination, i.e. $[PtL_2X_2]$ with L = 2-Apm, 4-phenyl-2-aminopyrimidine (4-Ph-2-Apm), 4-methyl-2-aminopyrimidine ($4\text{-}CH_3\text{-}2\text{-}Apm$), and 4-methoxy-2-aminopyrimidine ($4\text{-}CH_3O\text{-}2\text{-}Apm$), have been isolated.[116,147,150,151] The non-electrolytic character of the complexes has been demonstrated by measuring the molar conductances of their dimethylformamide (DMF) solutions (13 to

15 Ω^{-1} cm^2 mol^{-1}).[147] The far IR spectra show two absorption bands in the region of Pt–X stretching vibrations: 330–340 cm^{-1} (Cl), 231–249 cm^{-1} (Br), and 202–218 cm^{-1} (I), as well as two bands in the Pt–N region (257–290 cm^{-1}), which led to the conclusion that the complexes have the *cis*-configuration. On heating, the complexes isomerise to the *trans*-forms, whose spectra have a single narrow absorption band in the ν_{as}(Pt–X) and ν_{as}(Pt–N) regions. The *cis*-isomers exhibit a definite antitumour effect: in relation to adenocarcinoma AK-755, the inhibition of tumour growth was ~60%.[152] There exist divergent views about the geometrical structure of the non-electrolytic platinum(II) complexes of aminopyrimidines of analogous composition apparently due to the lability of these compounds.[153–155]

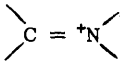
Charged complexes with monodentate coordination of 2-aminopyrimidine have been described: the isomeric $[Pt(NH_3)_2L_2]X_2$ and *cis*-$[PtenL_2]X_2$, where L = 2-Apm or 4-Ph-2-Apm and X = Cl^-, NO_3^-, or $\frac{1}{2}[PtCl_4]^{2-}$.[147,148] In order to synthesise chloride complexes with 2-Apm, the isomeric $[Pt(NH_3)_2Cl_2]$ and $[PtenCl_2]$ complexes were dissolved in an aqueous solution of the ligand, while the nitrate complexes were synthesised by treating the aquo-complexes $[Pt(NH_3)_2(H_2O)_2]^{2+}$ and $[Pten(H_2O)_2]^{2+}$ with the ligands; the platinites were precipitated with a $K_2[PtCl_4]$ solution. In order to determine the structure of the complexes, their IR and ^1H and ^{13}C NMR spectra were investigated. Coordination leads to an increase of the stretching vibration frequencies of the pyrimidine ring, which indicates the involvement of one of the heterocyclic nitrogen atoms in binding. Comparison of the ^1H NMR spectra of the ligands and complexes (Table 1) finally demonstrates this. The ^1H NMR spectrum of 2-aminopyrimidine shows a triplet signal due to the H(5) proton and a doublet signal due to the equivalent H(4) and H(6) protons. On coordination, the signals of all the protons undergo a downfield shift owing to deshielding.[148,149] The H(5) triplet signal shifts only slightly under these conditions, while the equivalence of the H(4) and H(6) protons breaks down and their signals become of the doublet of doublets type, which is due to the spin–spin interaction of the H(4) and H(6) nuclei both with H(5) and with one another. Such changes in the ^1H NMR spectra of the complexes agree with the formation of monodentate bonds by one of the heterocyclic nitrogen atoms, because, on coordination via the NH_2 group, the equivalence of the H(4) and H(6) protons would have been retained. The involvement of a heterocyclic nitrogen atom in binding is confirmed by the occurrence of the spin–spin interaction of the nearest proton with the ^{195}Pt nucleus. The ^1H NMR spectrum of 4-Ph-2-Apm in DMSO contains two doublets of equal intensity due to the non-equivalent H(5) and H(6) protons with a spin–spin coupling constant of 5 Hz (see Table 1), a singlet signal due to the NH_2 group (6.50 p.p.m.), and complex signals due to the protons of the phenyl group (7.40 and 7.94 p.p.m.). The coordination of 4-Ph-2-Apm in the platinum(II) sphere entails a downfield shift of the signals of the H(5) and H(6) protons, the H(6) doublet being displaced to a greater extent than the H(5) doublet. This permits the conclusion that the coordinate bond of 4-Ph-2-Apm is formed via the ring N(1) atom. An analogous conclusion has been reached on the basis of the ^{13}C NMR spectra of the platinum(II) complexes of 2,6-dimethyl-4-aminopyrimidine.[156–158] The signals of the C(6) carbon atoms ($\Delta\delta$ = 8–12 p.p.m.) and of the methyl groups in the vicinity of the N(1) atom, namely $C(2)H_3$ and $C(6)H_3$ ($\Delta\delta$ = 4–6 p.p.m.) undergo the greatest shift on coordination. The signal due to the protons of the NH_2 group undergoes a downfield shift (1.5–2.3 p.p.m.) and is broadened to a doublet. As in the complexes with cytosine,[129] this is explained by the partial double bond character of the  bond in the complex and the hindered nature of the rotation of the protons about this bond.

Table 1. The chemical shifts and the spin–spin coupling (SSC) constants of the protons of 2-aminopyrimidines in the free and coordinated states (X = Cl^- and NO_3^-)*.

Compound	Solvent	δ, p.p.m.				SSC constants, Hz		
		H (5)	H (4)	H (6)	$^3J_{5-6}$	$^3J_{5-4}$	$^4J_{4-6}$	$^3J_{^{195}Pt-^1H}$
2-Aminopyrimidine	D_2O	6 77	8.30	8.30	5,0	5.0	—	—
cis-$[Pt(NH_3)_2(2\text{-}Apm)_2]X_2$	D_2O	6.87	8.38	8,69	4.5	6.0	2,0	40
trans-$[Pt(NH_3)_2(2\text{-}Apm)_2]X_2$	D_2O	6.95	8.46	8.80	4,5	6.0	2.0	—
$[Pten(2\text{-}Apm)_2]X_2$	D_2O	6.87	8.38	8.69	4.5	6.0	2.0	40
2-Aminopyrimidine	DMF	6.50	8.13	8.13	5,0	5.0	—	—
cis-$[Pt(2\text{-}Apm)_2Cl]$	DMF	6.58	8.19	8.80	4,5	6.0	2.0	40
2-Amino-4-phenylpyrimidine	DMSO	7.04	—	8.26	—	5.0	—	—
cis-$[Pt(NH_3)_2(4\text{-}Ph\text{-}2\text{-}Apm)_2]Cl_2$	DMSO	7.32	—	8.72	—	7.0	—	—
trans-$[Pt(NH_3)_2(4\text{-}Ph\text{-}2\text{-}Apm)_2]Cl_2$	DMSO	7.41	—	8.85	—	7,0	—	—
$[Pten(4\text{-}Ph\text{-}2\text{-}Apm)_2]X_2$	DMSO	7.32	—	8,72	—	7.0	—	—
trans-$[Pt(4\text{-}Ph\text{-}2\text{-}Apm)_2Cl_2]$	DMSO	7.20	—	8.76	—	7,0	—	—

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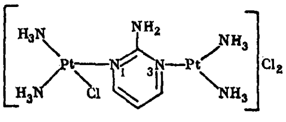
*The chemical shifts listed in the Table refer to the average positions of the proton signals.

Monodentate coordination via one of the heterocyclic nitrogen atoms is possible also for the aminopyrimidinium cation LH^+ protonated at the amino-group: the compounds $[MLHX_3]$ (X = Cl^- or Br^-; L = 2,6-dimethyl-4-aminopyrimidine or thiamine; M = Pt(II) or Pd(II)] have been isolated.[156–158]

Comparison of the spectroscopic (^1H NMR and electronic spectra) characteristics of the isomeric tetrammines $[PtA_2L_2]$.Cl_2 (A = NH_3; L = 2-Apm, 4-Ph-2-Apm, 4-CH_3-2-Apm, or 4-OCH_3-2-Apm) is of interest. It has been shown[159] that the downfield shift of the signal due to the non-labile H(4), H(5), and H(6) protons on coordination is greater for the *trans*-isomer than for the *cis*-isomer. The hyperchromic effect involving the absorption band of the ligands, observed on coordination, is also more pronounced for the *trans*-form. On this basis, it has been concluded that the *trans*-influence of 2-Apm and of its 4-substituted derivatives is smaller than that of NH_3. The explanation of this phenomenon may be sought in the lower stability of the bonds between aminopyrimidines and platinum(II).

The reactions between the platinum(II) complexes and 2-aminopyrimidines for the ratio Pt/L = 2 are accompanied by the formation of dinuclear complexes with a bridging aminopyrimidine molecule.[149,160] Thus complexes with the *cis*-structure and the composition $[PtA_2ClLPtA_2Cl]Cl_2$ (A = NH_3 or $\frac{1}{2}$en; L = 2-aminopyrimidine) have been isolated. Comparison of the ^1H NMR spectra of the ligands and the complexes showed that the signals of all the non-labile protons undergo a downfield shift on coordination and to a greater extent for the H(4) and H(6) protons [$\Delta\delta(4,6)$ = 0.6 p.p.m.]. The equivalence of the protons in the complex is maintained, since they give rise to one doublet signal with doubled intensity. This finding indicates the symmetrical binding of the 2-aminopyrimidine molecules to platinum atoms via the N(1) and N(2) atoms:



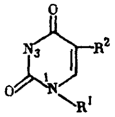
(XVIII)

The amino-group of the ligand in the complexes with bridge type coordination manifests weak acid properties [K_a = (1.8 ± 0.3) × 10^{-10}] as a consequence of the polarising influence of two neighbouring platinum(II) ions.[147]

The bidentate coordination of 2-aminopyrimidines with oxidation of the NH_2 group and the heterocyclic nitrogen atom is not characteristic of the platinum(II) complexes. The reactions of the platinum(II) complexes with 2-Apm in proportions of 1:1 lead to the formation of mixtures of compounds containing a dinuclear and a triammine complex.[159,161] On reaction with palladium (II), the compounds PdX_2.2-Apm (X = Cl^- or SCN^-), in which a chelate bond is postulated, were isolated.[162] In our view the formation of this bond is unlikely owing to the instability and strain of the four-membered ring. The molecular weights of the complexes should be measured, since they could have a dimeric structure with two bridging 2-aminopyrimidine molecules, i.e. $[PdX_2 2\text{-Apm}]_2$. The chelate coordination of 2-hydrazino-4,6-dimethylpyrimidine (2-hd-4,6-dmpm), observed by Saha et al.[163], is more probable, since this entails the formation of stable five-membered rings.

3. Platinum(II) Complexes of 2,4-Dioxopyrimidines

Among compounds of this class, the platinum(II) complexes of uracil (Ur), its nucleoside uridine (Urd), 5-methyluracil (thymine) (Th), its nucleoside thymidine (Thd), and also certain other 5- and 6-substituted uracils have been most thoroughly investigated.

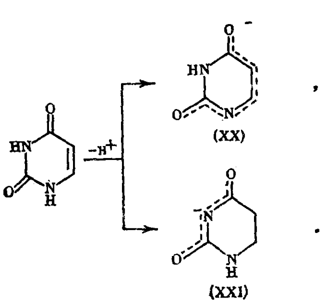


(XIX)

R^2 = H and R^1 = H(Ur) or β-D-ribofuranosyl (Urd); R^2 = CH_3 and R^1 = H(Th) or β-D-ribofuranosyl (Thd)

Uracil and thymine enter into the composition of natural biopolymers—RNA (Ur) and DNA (Th)—and can react with the antitumour complex *cis*-DDP. Active antitumour platinum complexes containing these ligands and other 2,4-dioxopyrimidines—the so called "platinum pyrimidine blues"—have been isolated.[164,165,166] The "blues" are more soluble in water and are less toxic than *cis*-DDP: LD_{50} is 200 to 500 mg kg^{-1} for the "blues" and 12 mg kg^{-1} for *cis*-DDP. The structure of the "blues" has not been fully established but it has been shown by the electrophoretic, chromatographic, and spectroscopic ("EXAFS") methods that they are cationic oligomeric platinum complexes with a molecular weight of 1000–3000 and a mixed oxidation state of platinum (2+ and 3+).[164,167] The ligands play the role of a bridge and join together the platinum atoms via heterocyclic atoms and O(4).

Uracil and its analogues exist in various tautomeric forms and exhibit ambident properties; for example, the two tautomeric forms (XX) and (XXI) are possible for the uracil anion:



The determination of the structure of the complexes with these ligands is therefore complicated and requires the application of a series of physical methods. In the absence of direct X-ray diffraction data, the most reliable information about the mode of coordination of these ligands can be obtained by NMR methods.

(a) Platinum(II) Complexes of Uracil, Thymine, and Their Nucleosides

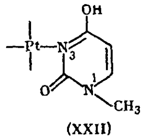
In contrast to the nucleic acid bases determined previously, uracil, thymine, and their nucleosides do not react with *cis*-DDP in a neutral medium.[13,26,37,168] The ability to be coordinated in the platinum(II) sphere is characteristic solely of the uracil and thymine anions and is associated with the manifestation by the latter of acid properties, which cytosine does not possess. The pK_a are 9.4 for uracil, 9.2 for uridine, 9.8 for thymine, and 9.7 for thymidine. The uracil and thymine monoanions consist of approximately equal amounts of forms dissociated at N(3)H and N(1)H.[169,170] As a result of tautomerism, the coordinate bonds linking uracil and thymine are formed both via the N(3) atom and the N(1) atom. Thus the reaction of the cation $[Pt(NH_3)_2.(H_2O)_2]^{2+}$ with uracil in a neutral medium leads to the formation of complexes with both types of bonds, via the N(3) and N(1) atoms, and having the composition $[Pt(NH_3)_2(Ur-H).NO_3]$.[171] The uridine and 6-uracil anions, in which the N(1) atoms is either linked to D-ribose or is blocked by the neighbouring methyl group, are coordinated solely via the N(3) atom.[110,163]

Complexes with the thymidine anions having the composition $[Pt(NH_3)_3(Thd-H)]NO_3$ and $[Pten(Thd-H)_2]$ have been isolated in reactions of thymidine with the corresponding aquo-complexes.[172] Thymidine is coordinated via the N(3) atom, which is accompanied, analogously to the behaviour observed in the complexes with the uracil and uridine anions,[171] by an upfield shift of the H(6) proton signal. The authors determined the formation constant of $[Pt(NH_3)_3(Thd-H)]^+$ ($\lg K_{form}$ = 10.4 ± 0.1) and the successive formation constants of $[Pten(Thd-H)_2]$ ($\lg K^1$ = 10.3 ± 0.1 and $\lg K^2$ = 7.4 ± 0.1) from the dependence of the intensity of the H(6) signal on the pH. The ^{13}C NMR method was used to determine the donor atom in solutions of $[PtenCl_2]$ with an excess of uridine or thymidine.[173] Two sets of signals due to carbon atoms can be observed in these systems, one referring to non-coordinated uridine or thymidine and the other to the complexes $[Pt(L-H)_2]$, where (L − H) are the uridine and thymidine anions. The greatest shift on coordination of uridine (compared with the non-bonded neutral molecule) is observed for the C(2) and C(4) atoms: their signals have undergone downfield shifts of 5.3 and 8.0 p.p.m. respectively. The C(5) and C(6) signals are displaced to a lesser extent and in the opposite direction—upfield.

A large series of studies on the platinum complexes of uracil and its derivatives have been carried out by Lippert and co-workers. The difficulty of determining the structure of the platinum complexes of unsubstituted uracil and thymidine, for which there is a possibility of the coordination of both tautomeric forms, was noted. In order to determine the type of coordination, IR and NMR spectroscopy are used.[174-177] Thus the stretching vibration frequency $\nu(C-O)$ for the complexes with the Pt–N(1) bond is characterised by an intense band at 1640 cm^{-1} with shoulders in close proximity to regions at lower and higher frequencies, while the Pt–N(3) bond is characterised by a band at 1550 cm^{-1} and another at 1650 cm^{-1}. The ^1H NMR spectra of the tautomeric complexes differ by the triplet splitting of the H(6) proton signal on formation of the Pt–N(1) bond ($^3J_{^1H-^{195}Pt}$ = 38–40 Hz), while in the spectra of the complexes with the Pt–N(3) bond the H(6) signal is not split while the H(5) signal is split but has a smaller spin–spin coupling constant ($^4J_{^1H-^{195}Pt}$ = 4–15 Hz). It has also been stated that the tautomers have different reactivities—the complexes with the Pt–N(1) bond are stable in an acid medium but at the same time they exchange the H(5) proton for deuterium, while the complexes with the Pt–N(3) bond split off the free ligand on heating in an acid medium. The exchange of H(5) with deuterium is observed in an alkaline medium in this case.[110] Factors influencing the formation of a particular tautomeric complex are said to include the nature of the solvent, the pH of the aqueous solution, the solubility of the reaction products, the capacity of the ligands for participation in a hydrogen bond, and even the reaction conditions.

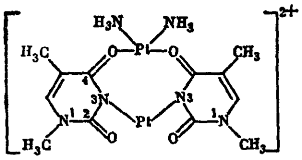
(b) Platinum(II) Complexes of N(1)-Substituted Uracil and Thymine

This class of compounds includes the uracil and thymine nucleosides and N(1)-methyl-substituted compounds. In many cases studies have been made of the reactions of 1-methyluracil and 1-methylthymine with platinum(II) complexes. The structure of these compounds can be established more readily than that of the complexes with unsubstituted ligands—the Pt–N(3) bond is formed in all cases. The reactions of the anions of 1-methyluracil and 1-methylthymine led to the isolation of the non-electrolytic complexes cis-$[Pt(NH_3)_2(1\text{-}CH_3Ur\text{-}H)_2].4H_2O$ and cis-$[Pt(NH_3)_2.(1\text{-}CH_3Th-H)_2]$,[176-178] the mixed type cationic complexes cis-$[Pt(NH_3)_2(1\text{-}CH_3Th-H)L]ClO_4$ (L = cytosine, guanine, or adenine),[179,180] and even complexes containing not only ligand anions but also ligand molecules—cis-$[Pt(NH_3)_2.(1\text{-}CH_3Ur)(1\text{-}CH_3Ur-H)]X.H_2O$.[181] It is suggested that the neutral ligand is coordinated in an unusual tautomeric form (XXII):

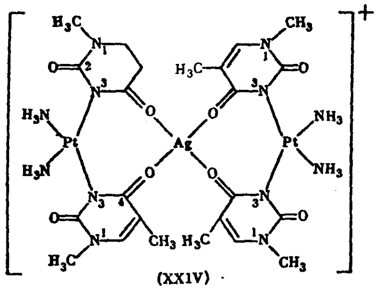

(XXII)

The Pt–N(3) bond with a neutral ligand is unstable, the ligand is readily split off, and X^- enters into the composition of the complex.

Polynuclear complexes with 1-methyluracil and 1-methylthymine can be formed via bridging hydroxo-groups or ligand anions. Dimers of the first type, namely cis-$[Pt.(NH_3)_2(L-H)]_2OH$, are formed in an alkaline solution. It has been suggested that the cis-Pt–OH–Pt group is capable of interacting with DNA bases, cross linking them via intrastrand or interstrand mechanisms.[180] Polymerisation via bridging 1-methyluracil and 1-methylthymine anions leads to the formation of homopolynuclear and heteropolynuclear complexes.[181-188] Exocyclic oxygen atoms participate in the bridge bond together with the heterocyclic nitrogen atoms. An example of a homonuclear polymer is the dimer cis-$[Pt(NH_3)_2(1\text{-}CH_3Th-H)]_2(NO_3)_2$ [182-184] with electron-donating N(3) and O(4) atoms [compound (XXIII)]:


(XXIII)

The bidentate bridge bond via the 1-methylthymine and 1-methyluracil anions exists also in heteronuclear complexes of the type Pt_2M, where M = Ag^+,[186] Mn^{2+},[187] or Cu^{2+},[188] for example in cis-$[Pt(NH_3)_2(1\text{-}CH_3Th-H)_2Ag(1\text{-}CH_3Th-H)_2.Pt(NH_3)_2]NO_3$ (XXIV):


(XXIV)

More complex polymeric structures occur when the 1-methyluracil anions exhibit the properties of tridentate ligands being coordinated via the N(3) atom and both exocyclic O(4) and O(2) atoms. An example is provided by the pentanuclear heteronuclear complex of the type Pt_4A_9 – $[Pt_4(NH_3)_8(1\text{-}CH_3Ur-H)_4Ag](NO_3)_5$.[189] After slight heating, the complex gives rise to the blue product $[Pt_4.(NH_3)_8(1\text{-}CH_3Ur-H)_4](NO_3)_5.5H_2O$, in which platinum is in the 2.25+ oxidation state. This product may be formed as a result of the intermolecular oxidation-reduction reaction

$$Ag^{+1}+e\rightarrow Ag^0,\ Pt_4^{8+}-e\rightarrow Pt_4^{9+}$$

The platinum "blues" incorporating the 1-methyluracil anions are obtained also after cautious oxidation of the "head to head" dimer $[Pt(NH_3)_2(1\text{-}CH_3Ur-H)]_2(NO_3)_2$ with nitric acid.[183,185] After more far reaching oxidation, yellow-orange diamagnetic complexes, resembling the platinum(III) dimers with α-pyridone, are formed.[190-192] Platinum "blues' with the thymine anion have also been described.[193]

The ^{195}Pt NMR method combined with high performance liquid chromatography has been used to determine the structure of the platinum(II) complexes of 1-methyluracil [89,194] (Table 2). The spectra of the mononuclear complexes show a single signal whose position is determined by the nature of the electron-donating atoms. Thus the replacement of two H_2O molecules by two Cl^- ions leads to an upfield shift c 500 p.p.m. An even greater upfield shift (820 p.p.m.) is observed after the replacement of two H_2O molecules by two 1-methyluracil anions. Complexes with the PtN_4 coordinatio unit, namely cis-$[Pt(NH_3)_2(1\text{-}CH_3Ur-H)_2]$ (–2407 p.p.m.) and $[Pt(NH_3)_4]^{2+}$ (–2579 p.p.m.) are characterised by the greatest upfield chemical shifts. The dimer cis-$[Pt(NH_3)_2.(1\text{-}CH_3Ur-H)]_2^{2+}$ with an asymmetric "head to head" structure, in which one of the platinum atoms is involved in the

PtN_4 coordination unit while the other is in the PtN_2O_2 group, gives rise to two signals in the ^{195}Pt spectrum, i.e. at −2210 and −1267 p.p.m., which correspond to two types of coordination.

Table 2. The ^{195}Pt NMR spectra of platinum(II) 1-methyluracilate complexes in D_2O (external standard—Na_2PtCl_6).[89]

Complexes with *cis*-structure	^{195}Pt chemical shift, p.p.m.
cis-DDP	−2097
$[Pt(NH_3)_2(H_2O)_2]^{2+}$	−1588
$[Pt(NH_3)_2(1\text{-}CH_3Ur\text{—}H)_2]$	−2407
$[Pt(NH_3)_2(1\text{-}CH_3Ur\text{—}H)(H_2O)]^+$	−1999
$[Pt(NH_3)_2(1\text{-}CH_3Ur\text{—}H)Cl]$	−2261
$[Pt(NH_3)_2(1\text{-}CH_3Ur\text{—}H)]_2^{2+}$	−2210, −1267

(c) Platinum(II) Complexes of 5-substituted Uracils

In the reactions of *cis*-DDP and its aquo-form with the sodium and lithium salts of 5-substituted uracil, complexes having the *cis*-structure with one and two ligand anions were isolated: $[Pt(NH_3)_2(5\text{-RUr}-H)Cl]$ (R = H, Br, or NO_2) and $[Pt(NH_3)_2(5\text{-RUr}-H)_2]$ (R = H, F, Cl, Br, I, or NO_2).[195] The anionic form of the ligand in the complexes follows from their composition and has been confirmed by the similarity of the UV and IR spectra of the complexes in the initial salt. The type of coordination was determined by the ^1H and ^{13}C NMR methods in relation to complexes with two anions. In the spectrum of the complex with uridine—*cis*-$[Pt(NH_3)_2.(Urd-H)_2]$—in which coordination is possible only via the N(3) atom, the H(6) proton signal is a doublet, as in the free ligand, and has undergone an upfield displacement of 0.2 p.p.m. compared with uridine. Analogous ^1H NMR spectra have been observed also for *cis*-$[Pt(NH_3)_2(Ur-H)_2]$, *cis*-$[Pt(NH_3)_2(5\text{-FUr}-H)_2]$, and *cis*-$[Pt(NH_3)_2(5\text{-BrUr}-H)_2]$, for which coordination of the anions by the N(3) atom is also suggested. The ^1H NMR spectrum of the complex *cis*-$[Pt.(NH_3)_2(5\text{-}NO_2Ur-H)_2]$ has a different form: the H(6) signal is a triplet as a result of the spin–spin interaction with the ^{195}Pt nucleus and its upfield shift is 0.1 p.p.m. In the spectrum of the complex of 5-chlorouracil, two H(6) signals are observed—a singlet with $\Delta\delta$ = 0.32 p.p.m. and a triplet for which $\Delta\delta$ = 0.10 p.p.m. Both forms of coordination of the ligand, via the N(3) and N(1) atoms, have been proposed for this complex. The conclusions reached have also been confirmed by ^{13}C NMR:[196] in the complexes with the Pt–N(3) bond, the greatest downfield shifts on coordination are observed for the C(2) and C(4) atoms, while in those with the Pt–N(1) bond, the greatest shifts are for C(2) and C(6).

IV. KINETICS OF THE REACTIONS OF PURINE AND PYRIMIDINE BASES AND THEIR NUCLEOSIDES WITH PLATINUM(II) COMPLEXES

In order to characterise the reactivity of the platinum(II) complexes, it is of interest to investigate the kinetics of the reactions of these compounds with the purine and pyrimidine DNA bases and as well as their antimetabolites and nucleosides. Such a study has been carried out for the reactions of the diammines $[Pt(NH_3)_2Cl_2]$ and the isomeric triammines $[(PtNH_3)_2InoCl]Cl$ with inosine and cytidine.[197,198] The interaction of *cis*-DDP with inosine incudes two stages:

$$cis\text{-}[Pt(NH_3)_2Cl_2] + L \xrightarrow{k^1} cis\text{-}[Pt(NH_3)_2LCl]^+ + Cl^- , \qquad (1)$$

$$cis\text{-}[Pt(NH_3)_2LCl]^+ + L \xrightarrow{k^2} cis\text{-}[Pt(NH_3)_2L_2]^{2+} + Cl^- . \qquad (2)$$

The kinetics of the second stage were investigated initially, because it proceeds with substitution of only one chloride ion by inosine. The conductimetric method was used and the reaction was carried out under pseudo-first-order conditions in an excess of the entering ligand at 50 °C. The constant k^2_{obs} was calculated from the first-order kinetic equation and its dependence on the concentrations of the ligand and the Cl^- ions was determined. Analysis of the data permits a series of conclusions: (1) the reactions of the cytidine complexes are faster than those of the inosine complexes; (2) the incorporation of inosine in the platinum(II) complexes obeys a kinetic equation which differs from the equation for the insertion of NH_3 or amine: for inosine there is no linear relation between k_{obs} and the inosine concentration and k_{obs} diminishes with increase of the concentration of Cl^- ions. This type of dependence has been explained by the fact that inosine is inserted mainly in the hydrolysis product *cis*-$[Pt(NH_3)_2InoH_2O]^{2+}$ and that the reverse insertion of Cl^- ions in the monoaquo-complex competes with this process. The characteristic feature of inosine is manifested by the fact that the rate constant for the insertion of the bulky ligand is lower than the rate constant for the incorporation of Cl^- ions in the monoaquo-complex; (3) the quantity k^2_{obs} depends on the geometrical structure of the triammine: the substitution of the Cl^- ion in the *cis*-triammine is faster than in the *trans*-isomer, which indicates a weaker *trans*-influence of inosine than that of NH_3. The reactions of guanosine with the triammines $[Pt(NH_3)_3Cl]Cl$ and *cis*-$[Pt(NH_3)_2CytCl]Cl$ proceed analogously.[145,199]

The rate constant for the first stage k^1_{obs} was estimated on the basis of the experimental study of the rate of reaction of the isomeric platinum(II) diammines with inosine and the known constants k^2_{obs} for the second stage. The quantity k^1_{obs} was found by solving the kinetic equation for two consecutive irreversible first-order reactions by means of a program specially devised for the CM-4 computer. The quantity k^1_{obs} varies linearly in this instance with the concentration of inosine, which is associated with the greater contribution of the mechanism involving the direct nucleophilic substitution in stage 1. The ratio of the constants k^1_{obs} for the isomeric diammines is the reverse of the ratio of the constants k^2_{obs} for the triammines: $k^1_{obs}(trans) > k^1_{obs}(cis)$ as a consequence of the greater *trans*-influence of Cl^- compared with NH_3.

It has been shown by the spectrophotometric method that the interaction of labile and less stable palladium(II) triammines [PddienBr]Br with inosine proceeds via a more complex mechanism,[200] including not only the stage involving the reversible hydrolysis of Br^- ions but also the reversible substitution of Br^- ions and water molecules by inosine. The conclusions reached in a conductimetric study of the kinetics of the reaction of [PtdienBr]Br with inosine[201] are close to ours. The kinetics of the reaction of $[PdenCl_2]$ with inosine have been studied by the stopped flow method with spectrophotometric measurements.[202] Hydrolytic and direct substitution processes were taken into account in the reaction mechanism, but the formation of complexes with two inosine molecules, which is extremely probable in the presence of a (10–20)-fold excess of the ligand, was not considered.

A conductimetric kinetic study at 50 °C of the interaction of cytidine with the platinum(II) triammine *cis*-$[Pt(NH_3)_2.CydCl]Cl$, the isomeric $[Pt(NH_3)_2InoCl]Cl$ complexes, and the *cis*-non-electrolyte $[Pt(NH_3)_2Cl_2]$ has been carried out.[197,198] The insertion of cytidine in the complexes obeys, in contrast to inosine and guanosine, the rules observed for other ligands L in the reactions with platinum(II) complexes; $k_{obs} = k_1 + k_2[L]$, where k_{obs} is the pseudo-first order rate constant, k^1 the hydrolysis rate constant, and k^2 the rate constant for direct substitution. It follows from a comparison of the quantities k_{obs} for the same complexes at the same concentrations of the entering ligand that the reactions with cytidine are faster than those with inosine and are somewhat slower than the reactions with guanosine.[197,199] The constant k_{obs} for the reaction of cytidine with *cis*-$[Pt(NH_3)_2.$ $.InoCl]Cl$ is greater than for the reaction with the *trans*-isomer, which has been explained by the weaker *trans*-influence of inosine compared with NH_3. The interaction of cytidine with *cis*-$[Pt(NH_3)_2Cl_2]$ follows an analogous law, but is somewhat faster. The kinetic parameters of the first stage exceed by factors of 3 for k_1^1 and 200 for k_2^1 the corresponding values for the second stage. The interaction of bifunctional mono- and di-nuclear platinum(II) complexes with oligo- and poly-nucleotides has been investigated.[203,204] The complex *cis*-$[Pt(NH_3)_2(H_2O)(OH)]^+$ binds oligocytidine via the N(3) atom; the reaction product then forms interstrand bonds with the inosine polynucleotide (polyI) via the substitution of the OH^- group by the inosine molecule deprotonated at N(1).[204] The kinetics of the reactions of $[XPt\ dien-(CH_2)_6-dienPtY](NO_3)_n$ (n = 2–4, $X = H_2O$, $Y = H_2O$ or Br^-, or $X = Y = Br^-$) with inosine monophosphate (IMP) and polyI have been investigated spectrophotometrically.[205] The decrease of the reaction rate in the presence of Br^- ions indicates the dominant role of the hydrolytic mechanism. The increase of the rate constant on passing from IMP to polyI has been explained by the increased contribution of the S_N2 mechanism in the latter case.

New data on the problems dealt with in this review have been communicated in the reports at the XIVth International Conference on Coordination Chemistry in 1986. The necessity for a comparative study of the interaction of the isomeric dichlorodiammineplatinum(II) complexes with DNA and oligo- and polynucleotides was pointed out.[206–208] A number of studies were devoted to the synthesis and investigation of the structure and kinetics of the formation of "platinum blues" with 1-methyluracil and its derivatives.[209–211] Dinuclear platinum(III) complexes with bridging anions of uracil and its derivatives have been isolated.[177] Treatment of these compounds with an excess of 1-methyluracil and also oxidation of the dimeric platinum(II) complexes of this ligand with nitric acid led to the isolation of the unusual platinum(III) complexes $[Pt_2(NH_3)_4(C_5H_5N_2O_2)_3]Si_6NO_3.7H_2O$, in which the third 1-methyluracil anion is linked to platinum(III) via the C_5 atom.[212] A chelate platinum(IV) complex of cytosine has been isolated.[213] The platinum(II) complex of guanosine $[PtGuaCl_2H_2O]$ was found to exhibit anticancer activity.[214] The stabilities of the bonds of purine and pyrimidine nucleosides and their mononucleotides with palladium(II) via various electron-donating heterocyclic nitrogen atoms [N(7), N(1), and N(3)] have been compared using the ^1H NMR method.[215] The kinetics of the reactions of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with nucleic acid bases have been studied and it has been shown that the rate of insertion of the bases varies in the sequence guanine > adenine ≅ cytosine > thymine.[216]

In conclusion, we may note that the results of the study of the structure and properties of the platinum(II) complexes of the purine and pyrimidine bases and their nucleosides and antimetabolites can be used to establish a correlation between the structure of the platinum(II) complexes, their reactivity in relation to DNA, and their antitumour activity. The characteristics of the purine and pyrimidine bases and their derivatives as ligands are manifested in their ambident character and in their tendency to form homo- and hetero-polynuclear complexes with bridge bonds and metal–metal bonds. The data on the acid–base properties and the kinetic and thermodynamic stabilities of the platinum(II) complexes of the above ligands make it possible to characterise their behaviour in biological media with different acidities and chloride ion concentrations and to estimate the influence of coordination on the properties of these ligands and the effects of their mutual influence in the platinum(II) coordination sphere.

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Acyclic Alkoxy- and Aryloxy-phosphoranes

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The review gives a systematic account of the methods of synthesis, physical properties, structure, and reactivity of pentacoordinate phosphorus compounds having an acyclic structure and containing alkoxy- and aryloxy-substituents. The bibliography includes 91 references.

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I. INTRODUCTION

Phosphorus is undoubtedly outstanding among other Group V elements of the Periodic System as regards the number of compounds with different coordinations of the central atom which really exist and are being investigated. The compounds of pentacoordinate phosphorus (phosphoranes) occupy a special place in organophosphorus chemistry. Fundamental research into the mechanisms of the reactions of organophosphorus compounds has yielded convincing evidence for the existence of intermediates with pentacoordinate phosphorus in reactions of compounds of tricoordinate and tetracoordinate phosphorus.[1–6] The concept of metastable hydroxyphosphorane derivatives $(RO)_{5-n}P(OH)_n$, formed as intermediates, has been dominant in the study of the biochemical role of phosphate-containing coenzymes, for example ATP.[7–10]

The ability of the phosphorus atom to form covalent bonds with five ligands has long been known in the inorganic chemistry of phosphorus. The high stability of PF_5 and other fluorophosphoranes has received a detailed theoretical justification.[11–13] On the other hand, the chemistry of stable pentaorganophosphoranes, i.e. compounds in which the phosphorus atom is linked by σ-bonds to five organic substituents, has been developing vigorously only during the last 25 years. Among the studies which have stimulated the detailed investigation of organophosphoranes, mention must be made of the investigation of the mechanism of the hydrolysis of cyclic phosphates,[14] which made it possible for the first time to discover the important role which the presence of a cyclic fragment in the molecule plays in the stabilisation of organophosphoranes. Ramirez[1,15] established the rules governing the formation of cyclic alkoxyphosphoranes and the principles of their molecular structure and pointed out the possibility of their synthetic employment.

Until recently, much less was known about pentaorganophosphoranes with an acyclic structure despite the fact that the closest models of the intermediates in the majority of the reactions of organophosphorus compounds (OPC), including biochemical processes, are precisely phosphoranes with a phosphorus atom not involved in a ring.

In the series of acyclic pentaorganophosphoranes, alkoxy- and aryloxy-phosphoranes are best known. Several relatively unstable acyclic alkoxyphosphoranes with arylthio-groups[16,17] or dialkylamino-groups[18] as well as several penta(perfluoroalkyl)phosphoranes[19,20] and penta-arylphosphoranes[21] are known.

The increased stability of acyclic alkoxy- and aryloxyphosphoranes compared with their thia- and aza-analogues can apparently be explained by the greater electronegativity of the oxygen atom compared with the oxygen atoms attached to sulphur and nitrogen atoms. On the other hand, the electronic and steric properties of the substituents at the oxygen atoms could influence the stability and reactivity of the same phosphoranes. In order to elucidate the factors influencing the properties of acyclic alkoxyphosphoranes, methods have been developed in recent years for the synthesis of a wide variety of compounds of this type and their reactivity has been investigated in reactions with organic compounds of different classes. The results of these studies are surveyed in the present review.

II. METHODS OF SYNTHESIS

The methods of synthesis of alicyclic penta-alkoxy- and penta-aryloxy-phosphoranes, as well as alicyclic alkoxy- and aryloxy-organophosphoranes, can be usefully divided into three groups in terms of the coordination of the phosphorus in the initial compounds used for the synthesis. Many of these phosphoranes have been obtained from compounds of pentacoordinate and tricoordinate phosphorus and many fewer from compounds of tetracoordinate phosphorus.

1. Synthesis from Halogenophosphoranes

The reaction of phosphorus pentachloride and phenol proceeds, according to Anshutz[22] and Zhmurova and Kirsanov,[23] via a stage involving the formation of dichlorotriphenoxyphosphorane (I) and leads to an organophosphorus compound of a new type—pentaphenoxyphosphorane (II):

$$3C_6H_5OH + PCl_5 \xrightarrow[-3HCl]{} \underset{(I)}{(C_6H_5O)_3PCl_2}$$

$$(C_6H_5O)_3PCl_2 + 2C_6H_5OH \xrightarrow[-2HCl]{} \underset{(II)}{(C_6H_5O)_5P} \quad .$$

However, ^{31}P NMR [24] showed that these reactions yield not compound (II) but a mixture of dichlorotriphenoxyphosphorane (I) and other compounds.

Analytically pure pentaphenoxyphosphorane (II) was obtained only in the presence of a base—γ-collidine:[24]

$$PCl_5 \xrightarrow[2)\ 5C_6H_5OH]{1)\ 5(CH_3)_3C_5H_2N,0°C} \underset{(II)}{(C_6H_5O)_5P} + 5(CH_3)_3C_5H_2N \cdot HCl \quad .$$

Other substituted pentaphenoxyphosphoranes $(ArO)_5P$ with $Ar = o\text{-}CH_3C_6H_4$, $p\text{-}CH_3C_6H_4$, $o\text{-}ClC_6H_4$, or $p\text{-}ClC_6H_4$,[25] as well as penta(perfluorophenoxy)phosphoranes [26] have been obtained analogously.

A method consisting in the reaction of halogenophosphoranes with alcohols or phenols in the presence of bases and also with alkoxides, phenoxides, or alkoxy- and aryloxy-silanes has been used successfully for the synthesis of a whole series of acyclic alkoxy- and aryloxy-phosphoranes. Apart from PCl_5, the halogenophosphoranes employed were PF_5, alkyl-, and aryl-fluoro-phosphoranes,[27,28] alkoxychloro- and alkoxyfluoro-phosphoranes,[27,29–32] dibromotriphenyl- or dibromotributyl-phosphoranes,[33,34] and tris(trifluoromethyl)-fluoro- or tris(trifluoromethyl)chloro-phosphoranes [35,36] (Table 1):

$$(CH_3)(CF_3)_3PF + CH_3OSi(CH_3)_3 \xrightarrow[-(CH_3)_3SiF]{} \underset{(III)}{(CH_3)(CF_3)_3POCH_3}$$

$$R^1R^2_2PX_2 + 2R^3OM \xrightarrow[-2MX]{} \underset{(IV)-(XIX)}{R^1R^2_2P(OR^3)_2} \quad .$$

When phosphorus pentachloride is treated with perfluoro-t-butyl hypochlorite penta(perfluoro-t-butoxy)phosphorane is formed in a quantitative yield.[37]

2. Synthesis from Compounds of Tetracoordinate Phosphorus

There are very few methods of synthesis of acyclic alkoxy- or aryloxy-phosphoranes from compounds of tetracoordinate phosphorus. Methyl- or aryl-aryloxy-phosphoranes containing two, three, or four aryloxy-groups [compounds (XX)–(XXVI) and (XXIX)] are formed, for example, when methyl- or aryl-aryloxyphosphoniatrifluoromethanesulphonates (XXVII) [38–40] or trichlorophenylphosphonium chloride (XXVIII) [39] are treated with the corresponding phenoxides:

$$\underset{(XXVII)}{R_n\overset{+}{P}(OAr)_{4-n}\overline{S}O_3CF_3} + ArOM \xrightarrow[-CF_3SO_3M]{} \underset{(XX)-(XXIV)}{R_nP(OAr)_{5-n}}$$

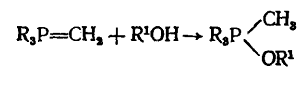
$R{=}CH_3$, $n = 1$, $Ar{=}C_6H_5$ (XX), $2,6\text{-}(CH_3)_2C_6H_3$ (XXI), $2\text{-}CH_3C_6H_4$ (XXII), $4\text{-}CH_3C_6H_4$ (XXIII); $R{=}CH_3$, $n = 2$, $Ar{=}2\text{-}CH_3C_6H_4$ (XXIV)

$$CH_3(C_6H_5)_n\overset{+}{P}(OC_6H_5)_{3-n}\overline{O}SO_2CF_3 \xrightarrow[-CF_3SO_3M]{C_6H_5OM} \underset{(XXV),\ (XXVI)}{CH_3(C_6H_5)_nP(OC_6H_5)_{4-n}}$$

$n = 1$ (XXV), 2 (XXVI)

$$\underset{(XXVIII)}{C_6H_5\overset{+}{P}Cl_3Cl^-} + 4C_6H_5OH \xrightarrow{2,6\text{-lutidine}} \underset{(XXIX)}{C_6H_5P(OC_6H_5)_4} \quad .$$

It has been established[41] that the alkoxytetramethylphosphoranes (XXX) and (XXXI) and the alkoxymethyltriphenylphosphoranes (XXXII)–(XXXIV) are formed as a result of the addition of alcohols to trimethylphosphinomethylene (XXXV) or triphenylphosphinomethylene (XXXVI) respectively:



$$R_3P{=}CH_2 + R^1OH \rightarrow R_3P\begin{matrix}\diagup CH_3\\ \diagdown OR^1\end{matrix}$$

$R{=}CH_3$ (XXXV), C_6H_5 (XXXVI)

$R{=}CH_3$, $R^1{=}CH_3$ (XXX), C_2H_5 (XXXI);
$R{=}C_6H_5$, $R^1{=}CH_3$ (XXXII),
C_2H_5 (XXXIII), $(CH_3)_2CH$ (XXXIV) .

The formation of acyclic alkoxy- and aryloxy-phosphoranes is possible in principle also as a result of the addition of suitable reagents to the P=O double bond. However, although several examples of addition to the phosphoryl group, involving both an increase of the coordination number of phosphorus[42] and proceeding without change in coordination,[43–48] are known at present in the chemistry of organophosphorus compounds, the only rigorously demonstrated instance of the synthesis of a pentacovalent phosphorane structure among

Table 1. The synthesis and properties of the alkoxyphosphoranes $R^1R^2_2PX_2 + 2R^3OM \xrightarrow[-2MX]{} \underset{(IV)-(XIX)}{R^1R^2_2P(OR)^3_2}$

No. of compound	R^1	R^2	R^3	X	M	M.p., °C, b.p., °C (mmHg)	δ, p.p.m.[c]	Refs.
(IV)	C_6H_5	C_6H_5	CF_3CH_2	Br	Na	—[a]	—	[33, 34]
(V)	C_6H_5	C_6H_5	$C_6H_5C(CF_3)_2$	Br	Na	124—126	—	[33]
(VI)	C_4H_9	C_4H_9	CF_3CH_2	Br	Na	—[a]	—	[34]
(VII)	CF_3	CF_3	CH_3	Cl, F	$Si(CH_3)_3$	—[a]	−74.5	[35]
(VIII)	$(CF_3)_2CHO$	CH_3	$(CF_3)_2CH$	Cl	Li	46—49	−20.3	[30]
(IX)	$(CF_3)_2CHO$	CF_3	$(CF_3)_2CH$	Cl	Li	45 (0.01)	−72.8	[30]
(X)	C_6H_5	$(CF_3)_2CHO$	$(CF_3)_2CH$	Cl	Li	91	−65.0	[30]
(XI)	C_6H_5	CF_3CH_2O	CF_3CH_2	F	$Si(CH_3)_3$	62	−58.7	[28]
(XII)	CH_3	$(CF_3)_2CHO$	$(CF_3)_2CH$	Cl	Li	33—37	−53.0	[30]
(XIII)	CH_3	CF_3CH_2O	CF_3CH_2	F	$Si(CH_3)_3$	—[a]	—	[28]
(XIV)	$(CF_3)_2CHO$	$(CF_3)_2CHO)$	$(CF_3)_2CH$	Cl	Li	25—28	−84.0	[29]
(XV)	CF_3CH_2O	CF_3CH_2O	CF_3CH_2	F	$Si(CH_3)_3$	44 (0.15)[b]	−76.6[b]	[27]
(XVI)	$HCF_2CF_2CH_2O$	$HCF_2CF_2CH_2O$	$HCF_2CF_2CH_2$	Cl, Br	H	88—89 (0.05)	−77.0	[32]
(XVII)	$H(CF_2CF_2)_2CH_2O$	$H(CF_2CF_2)_2CH_2O$	$H(CF_2CF_2)_2CH_2$	Cl, Br	H	159—161 (0.05)	−76.0	[32]
(XVIII)	CCl_3CH_2O	CCl_3CH_2O	CCl_3CH_2	Cl, Br	H	104—106	−79.6	[31]
				F	$Si(CH_3)_3$	122—124	−79.0	[27]
(XIX)	CCl_3CH_2O	CCl_3CH_2O	C_6H_5	Cl, Br	H	—[a]	−85.1	[31]

---

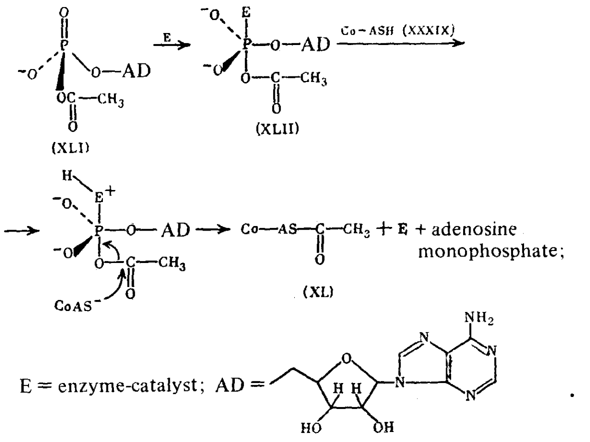
[a] Not isolated in a pure state. [b] Data quoted by Denney et al.[16] [c] In ^{31}P NMR (relative to 85% H_3PO_4).

the acyclic compounds is the reaction of tris(trifluoromethyl)-phosphine oxide (XXXVII) with hexamethyldisiloxane:[49,50]

$$\underset{\text{(XXXVII)}}{(CF_3)_3P{=}O} + (CH_3)_3SiOSi(CH_3)_3 \rightarrow \underset{\text{(XXXVIII)}}{(CF_3)_3P[OSi(CH_3)_3]_2}$$

The phosphorane (XXXVIII) formed under these conditions is a low-boiling liquid, which has been isolated in a pure state by vacuum distillation.

It is noteworthy that the hydroxyphosphorane concept, based on the hypothesis that processes involving adenosine triphosphate proceed via an intermediate with a pentacoordinate phosphorus atom,[8,9] formed as a result of the addition of the enzyme to the P=O bond, has become widely adopted at the present time in biochemistry. For example, in the conversion of the coenzyme A (CoASH) (XXXIX) into the acetylcoenzyme A (XL), the adenyl acetate (XLI) formed initially reacts with the enzyme E catalysing this process and is converted into the pentacoordinate intermediate (XLII). As a result of proton transfer from the mercapto-group of coenzyme A (XXXIX) to the apical atom through which the enzyme is linked to the phosphorus followed by attack on the carbonyl group by the coenzyme anion, acetylcoenzyme A (XL) is subsequently obtained:[9]



3. Synthesis from Compounds of Tricoordinate Phosphorus

As a result of the studies of Denney and co-workers, the method of synthesis of acyclic alkoxyphosphoranes from compounds of tervalent phosphorus and dialkyl peroxides has come to be widely known since 1964. The first representative of acyclic penta-alkoxyphosphoranes, namely pentaethoxyphosphorane (XLIII), was obtained by the reaction of triethyl phosphite with diethyl peroxide.[51] Subsequently pentamethoxyphosphorane (XLIV) was also obtained by the same method.[52] However, these compounds were not isolated in a pure state—they contained an admixture of trialkyl phosphates:

$$(AlkO)_3P + AlkOOAlk \rightarrow (AlkO)_5P;\ Alk{=}C_2H_5\ \text{(XLIII)},\ CH_3\ \text{(XLIV)}\ .$$

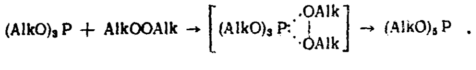
Having studied systematically the reaction of diethyl peroxide with compounds of tervalent phosphorus, Denney and co-workers[53-55] found the optimum conditions for the synthesis and isolation of a whole series of diethoxyphosphoranes (XLV)-(LIII):

$$R^1R^2_2P + C_2H_5OOC_2H_5 \rightarrow \underset{\text{(XLV)}-\text{(LIII)}}{R^1R^2_2P(OC_2H_5)_2}$$

$$R^1{=}R^2{=}C_6H_5\ \text{(XLV)},\ C_4H_9\ \text{(XLVI)},\ CH_3\ \text{(XLVII)},$$
$$(CH_3)_2CH\ \text{(XLVIII)},\ CH_3O\ \text{(XLIX)};\ R^1{=}C_2H_5O,\ R^2{=}C_6H_5\ \text{(L)};$$
$$R^1{=}CH_3,\quad R^2{=}C_6H_5\ \text{(LI)};\quad R^1{=}C_6H_5,$$
$$R^2{=}C_2H_5O\ \text{(LII)},\ CH_3\ \text{(LIII)}\ .$$

Denney and Jones[55] suggest two possible mechanisms for the formation of phosphoranes from dialkyl peroxides.

The direct formation of alkoxyphoshorane in a single stage via a transition state in which both oxygen atoms are linked to the phosphorus atom:



$$(AlkO)_3P + AlkOOAlk \rightarrow \left[(AlkO)_3P\begin{matrix}\cdot OAlk\\ |\\ \cdot OAlk\end{matrix}\right] \rightarrow (AlkO)_5P\ .$$

A two-stage mechanism involving substitution at the oxygen atom of the dialkyl peroxide with formation of the tetra-alkoxyphosphonium cation–alkoxide anion ion pair, which is subsequently converted into the penta-alkoxyphosphorane:

$$(AlkO)_3P + AlkOOAlk \rightarrow (AlkO)_4\overset{+}{P}AlkO^- \rightarrow (AlkO)_5P$$

The reactivity of phosphites and phosphines in relation to diethyl peroxide is the opposite of their reactivity in nucleophilic substitution reactions with C_2H_5L.[55] These data make it possible to give preference to the single-stage mechanism of the formation of the phosphorane in which the tervalent phosphorus atom is inserted, as a biphilic reagent, in the oxygen–oxygen bond.

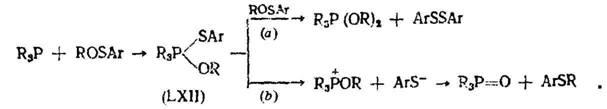
The disadvantages of using dialkyl peroxides are the difficulty of obtaining them, their explosive nature, and also the limited set of such compounds. The reactions with dialkyl peroxide take place slowly [for example, in the synthesis of pentaethoxyphosphorane (XLIII) the reaction lasts 20 days at room temperature[55]] and the phosphoranes are always formed not in a pure state but in a mixture with the oxidation products of the initial organophosphorus compound: phosphates, phosphonates, phosphinates, or tertiary phosphine oxides.[51-55]

The method of synthesis of acyclic alkoxyphosphoranes involving the reaction of derivatives of tervalent phosphorus with alkyl benzenesulphenates is free from many of these disadvantages. When this method involving the reaction of two moles of alkyl benzenesulphenate with tervalent phosphosus compounds under mild conditions is used, the corresponding alkoxyphosphoranes (IV), (XI), (XV), (XLIII)-(XLV), (L), (LII), and (LIV)-(LXI) are formed in high yields:[16,56-59]

$$(C_6H_5)_{3-n}P(OAlk)_n + 2AlkOSC_6H_5 \rightarrow \underset{\text{(IV), (XI), (XV), (XLIII)}-\text{(XLV), (L), (LII), (LIV)}-\text{(LXI)}}{(C_6H_5)_{3-n}P(OAlk)_{n+2}} + (C_6H_5S)_2$$

$$n=0,\ Alk{=}CF_3CH_2\ \text{(IV)},\ CH_3CH_2\ \text{(XLV)};$$
$$n=1,\ Alk{=}CH_3CH_2\ \text{(L)},\ CF_3CH_2\ \text{(LXI)};$$
$$n=2,\ Alk{=}CF_3CH_2\ \text{(XI)},\ CH_3CH_2\ \text{(LII)},\ \text{cyclo-}C_5H_9\ \text{(LIX)},\ (CH_3)_3CCH_2\ \text{(LX)};$$
$$n=3,\ Alk{=}CF_3CH_2\ \text{(XV)},\ CH_3CH_2\ \text{(XLIII)},\ CH_3\ \text{(XLIV)},\ (CH_3)_2CH\ \text{(LIX)},$$
$$(CH_3)_3CCH_2\ \text{(IV)},\ \text{cyclo-}C_5H_9\ \text{(LVI)},\ \text{cyclo-}C_6H_{11}\ \text{(LVII)},\ C_6H_5CH_2\ \text{(LVIII)}\ .$$

It has been suggested[56-60] that the mechanism of this reaction involves the direct insertion of phosphorus in the S–O bond analogous to the reaction with dialkyl peroxides[55,61] with a certain degree of donation of the free electron pair of sulphur to the phosphorus orbitals in the transition state and the formation of alkoxyarylthiophosphorane (LXII) as an intermediate. Such mixed alkoxyarylthiophosphoranes have been isolated in the reactions of alkyl benzenesulphenates with cyclic phosphites[56,62] and in other cases in reactions with acyclic tris(2,2,2-trifluoroethyl)[16] and tris(1-trifluoromethyl-2,2,2-trifluoroethyl) phosphites.[63] The alkoxyarylthiophosphorane (LXII) then reacts with another molecule of benzenesulphenate to form a dialkoxyphosphorane and diphenyl disulphide (pathway *a*):



(LXII)

The other pathway in the reactions of tervalent phosphorus compounds with alkyl benzenesulphenates involves the formation of a phosphoryl compound and an alkyl aryl sulphide, apparently as a result of the dissociation of the mixed alkoxyarylthiophosphorane (LXII) into an ion pair and its subsequent reactions (pathway *b*). For example, diethoxyphenylphosphine reacts with ethyl benzenesulphenate to form 65% of tetraethoxyphenylphosphorane (LXII) and 35% of diethyl phenylphosphonate.[59] On the other hand, the reactions of mixed alkylarylphosphines[55] and tributylphosphine[60] with alkyl benzenesulphenates proceed only via pathway *b*. Apparently, the presence of electron-donating alkyl groups promotes the stabilisation of the phosphonium cation.[54] If, on the other hand, the rate of the reaction of the mixed alkoxyarylthiophosphorane with another molecule of alkyl benzenesulphenate is higher than the rate of its dissociation, pathway *a* operates.

Apart from the two general methods of synthesis of acyclic alkoxyphosphoranes from tricoordinate phosphorus compounds described above, several individual instances of the synthesis of phosphoranes of this type are also known.

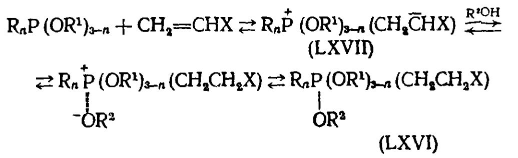
Pentakis(2,2,2-trifluoroethoxy-1-trifluoromethyl)phosphorane (XIV) has been obtained by the reaction of the phosphite (LXIII) with the bis(1,1,1,3,3,3-hexafluoroisopropyl) ester of sulphoxylic acid (LXIV):[64]

$$\underset{\text{(LXIII)}}{4\,[(CF_3)_2CHO]_3P} + \underset{\text{(LXIV)}}{S[OCH(CF_3)_2]_2} \rightarrow \underset{\text{(XIV)}}{[(CF_3)_2CHO]_5P} +$$
$$+ 2\,[(CF_3)_2CHO]_3P{=}S + [(CF_3)_2CHO]_3P{=}O + (CF_3)_2CHOCH(CF_3)_2 \ .$$

The reaction of chloroform with sodium methoxide and trimethyl phosphite leads to the formation of tetramethoxydimethoxymethylphosphorane (LXV):[65]

$$(CH_3O)_3P + CHCl_3 + 3CH_3ONa \rightarrow \underset{\text{(LXV)}}{(CH_3O)_4PCH(OCH_3)_2} + 3NaCl \ .$$

Aryl phosphonites and aryl phosphinates react with derivatives of acrylic acid in the presence of alcohols to form alkoxyphosphoranes (LXVI):[66]



$$R_nP(OR^1)_{3-n} + CH_2{=}CHX \rightleftarrows \underset{\text{(LXVII)}}{R_n\overset{+}{P}(OR^1)_{3-n}(CH_2\overset{-}{C}HX)} \xrightleftharpoons{R^2OH}$$
$$\rightleftarrows R_n\underset{\underset{-OR^2}{\vdots}}{\overset{+}{P}}(OR^1)_{3-n}(CH_2CH_2X) \rightleftarrows R_n\underset{\underset{OR^2}{|}}{P}(OR^1)_{3-n}(CH_2CH_2X)$$

(LXVI)

$n = 1, 2$; $R{=}C_6H_5$; $R^1 = CH_3$, C_2H_5;
$R^2 = CH_3$, C_2H_5, $(CH_3)_3C$;
$X{=}COOC_2H_5$, CN
$n = 2$; $R{=}n\text{-}(CH_3)_3COC_6H_4$; $R^1{=}R^2{=}(CH_3)_3C$; $X{=}COOC_2H_5$.

It has been suggested[66] that the betaine (LXVII) formed as an intermediate is protonated by alcohol and the alkoxide anion then carries out a nucleophilic attack on the positively charged phosphorus atom with formation of the phosphoranes (LXVI).

III. NMR SPECTRA AND STRUCTURE

The signals of the phosphorus nuclei in the ^{31}P NMR spectra of acyclic alkoxy- and aryloxy-phosphoranes are in the range δ_P = −20.3−−92.0 p.p.m. (relative to 85% H_3PO_4). The chemical shifts at the highest fields are characteristic of penta-alkoxy- and penta-aryloxy-phosphoranes. When one, two, or three alkoxy-groups are replaced by an aryl group and especially by the methyl group, the chemical shift undergoes an appreciable downfield displacement (Table 2). It may be that such displacement is caused by the distortion of the symmetry of the electron distribution around the pentacoordinate phosphorus induced by the difference between the electronegativities of the alkyl(aryl) and alkoxy-substituents. With a decrease in the difference between the electronegativities of the substituents—in the case of the phosphoranes (VII), (IX), and (XXXVIII) containing CF_3 groups at the phosphorus atom—there is almost no downfield displacement of the signal. A similar hypothesis has been used to account for the downfield displacement of the signals in the ^{31}P NMR spectra of tetracoordinate phosphorus compounds.[67] An exception in the series considered is that of alkoxytetramethylphosphoranes (XXX) and (XXXI), whose chemical shifts occur at the lowest fields (Table 2).

Table 2. ^{31}P NMR spectra of alkoxy- and aryloxy-phosphoranes.

Formula	δ_P, p.p.m.	Refs.
$P(OCH_3)_5$ (XLIV)	−66.0	[57]
$P(OC_2H_5)_5$ (XLIII)	−70.9	[51]
$P(OCH_2CF_3)_5$ (XV)	−76.6	[16]
$P[OCH(CF_3)_2]_5$ (XIV)	−84.5	[29]
$P(OCH_2CF_2CF_2H)_5$ (XVI)	−77.0	[32]
$P(OCH_2CF_2CF_2CF_2CF_2H)_5$ (XVII)	−76.0	[32]
$P(OCH_2CCl_3)_5$ (XVIII)	−79.6	[31]
$P(OC_6H_5)_5$ (II)	−85.4; −84.2[a]	[70]
$C_6H_5P(OC_2H_5)_4$ (LII)	−55.0	[54]
$C_6H_5P(OCH_2CF_3)_4$ (XI)	−61.7	[16]
$C_6H_5P[OCH(CF_3)_2]_4$ (X)	−65.0	[30]
$CH_3P[OCH(CF_3)_2]_4$ (XII)	−53.0	[30]
$(C_6H_5)_2P(OC_2H_5)_3$ (L)	−41.0	[54]
$(C_6H_5)_2P(OCH_2CF_3)_3$ (LXI)	−42.5	[16]
$(CH_3)_2P[OCH(CF_3)_2]_3$ (VIII)	−20.3	[30]
$(CF_3)_2P[OCH(CF_3)_2]_3$ (IX)	−72.8	[30]
$(C_6H_5)_3P(OC_2H_5)_2$ (XLV)	−54.0	[53]
$(C_6H_5)_3P(OCH_2CF_3)_2$ (IV)	−58.2	[16]
$(C_6H_5)_2(CH_3)P(OC_2H_5)_2$ (LI)	−47.0	[54]
$(C_6H_5)(CH_3)_2P(OC_2H_5)_2$ (LIII)	−40.0	[54]
$(CH_3)_3P(OC_2H_5)_2$ (XLVII)	−39.0	[54]
$(CF_3)_3P(OCH_3)_2$ (VII)	−64.5	[35]
$(CF_3)_3P[OSi(CH_3)_3]_2$ (XXXVIII)	−92.8	[50]
$(CH_3)_4POCH_3$ (XXX)	−88.0	[41]
$(CH_3)_4POC_2H_5$ (XXXI)	−92.0	[41]

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[a] In the solid state.

It has been suggested that penta-alkoxyphosphoranes have the structure of a trigonal bipyramid (TBP). However, ^{1}H, ^{13}C, and ^{19}F NMR studies of a series of these compounds [compounds (IV)–(VII), (XV), and (XVIII)] [26,57,68,69] demonstrated the equivalence of the alkoxy-groups even at low temperatures. This has been explained[57] by the very low barrier to permutational isomerisation of the phosphoranes investigated.

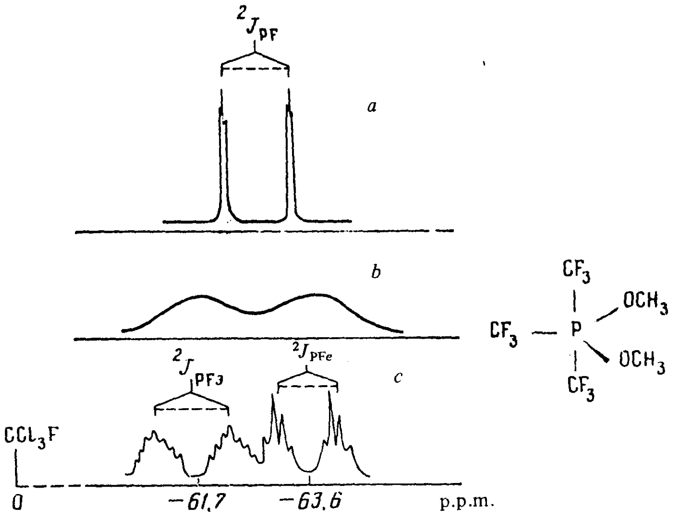
It has been established by X-ray diffraction [71] that pentaphenoxyphosphorane in the crystalline state has the structure of a TBP with the phosphorus atom at the centre. The two axial P–O bonds (1.602, 1.596, and 1.600 Å). It has been suggested that the electrons of the apical oxygen atoms are less involved in the p, d_π conjugation with the phosphorus atom than the electrons of the equatorial oxygen atoms and are mainly delocalised over the benzene rings. The five benzene rings are distributed in the TBP in such a way that the intramolecular repulsion is a minimum.

In the case of tetrakix(2,6-dimethylphenoxy)methylphosphorane (XXI) [38] and tetrakis(1,1,1,3,3,3-hexafluoroisopropoxy)methylphosphorane (XII), [30] the rate of pseudorotation is reduced to such an extent that, in the ^{1}H NMR spectra of the phosphorane (XXI) at −65 °C and in the ^{1}H and ^{19}F NMR spectra of the phosphorane (XII) even at 25 °C, the alkoxy-substituents are found to be non-equivalent owing to their location in the axial or equatorial positions.

The study of the ^{1}H and ^{19}F NMR spectra of a series of alkyl- and aryl-phosphoranes (XLV), (XLVI), and (L) at different temperatures showed that the rate of the pseudotransformation is a function of the number of alkyl or aryl groups linked directly to the phosphorus. The pseudotransformation is retarded when the number of these groups increases. [55]

The trigonal-bipyramidal structure of trialkoxy- and triaryloxy-phosphoranes, in which two alkoxy- or aryloxy-groups occupy axial positions and one occupies an equatorial position, has been established spectroscopically for triethoxydiphenylphosphorane (L) at −60 °C, [56] dimethyltri(2-methylphenoxy)phosphorane (XXIV) at −95 °C, [38] diphenyltris(2,2,2-trifluoro-1-trifluoromethylethoxy)phosphorane (VIII) at 25 °C. [30]

The activation energies for the intramolecular pseudorotation of the ligands are 5.8, 12.0, and 14.0 kcal mol^{-1} respectively for the phosphoranes (XXIV), (L), and (LXI).



^{19}F NMR spectra of dimethoxytris(trifluoromethyl)phosphorane (VII) in CCl$_3$F: [35] *a*) $t = 33°$, $^2J_{PF} = 96$ Hz; *b*) $t = -60$ °C; *c*) $t = -80$ °C, $^2J_{PF_e} = 108$ Hz and $^2J_{PF_a} = 88$ Hz.

Dimethyltris(2,2,2-trifluoro-1-trifluoromethylethoxy)phosphorane (VIII) has apparently an even higher isomerisation barrier, because the coalescence temperature for this compound is 60 °C. [30] The ^{1}H NMR spectra of the phosphoranes (XLV) and (LI) (Table 2) do not change in the temperature range from −60° to 120 °C or to 60° respectively. It has been suggested [54] that in these compounds and also in the phosphorane $(C_6H_5)_3(OCH_2CF_3)_2$ (V) [34] the alkoxy-groups occupy axial positions and the phenyl and alkyl groups occupy equatorial positions. The invariance of the NMR spectra over a wide temperature range can apparently be explained by the high energy barrier to pseudorotation.

In contrast to the phosphoranes (IV), (XLV), and (LI), the alkoxy-groups in dimethoxytris(trifluoromethyl)phosphorane (VII) are in the equatorial positions, which follows from the analysis of the ^{19}F NMR spectra (see Figure). At room temperature, the CF$_3$ groups are equivalent and appear in the ^{19}F NMR spectrum as a doublet of heptets. When the temperature is reduced to −80 °C, two signals with an intensity ratio of 2 : 1 are observed in the ^{19}F NMR spectrum—a doublet of quartets with $\delta_F = -63.6$ p.p.m. and relatively small spin–spin coupling constants ($^2J_{PF} = 88$ Hz), which are characteristic of axial CF$_3$ groups, and a doublet of heptets with $\delta_F = -61.7$ p.p.m. and relatively higher values of the spin–spin coupling constants ($^2J_{PF} = 108$ Hz) characteristic of equatorial CF$_3$ groups. [35]

An analogous trigonal bipyramidal structure with two axial CF$_3$ groups has been determined by ^{19}F NMR also for tris(trifluoromethyl)bis(trimethylsiloxy)phosphorane (XXXVIII) [49,50] and also for methoxymethyltris(trifluoromethyl)phosphorane (III). [36]

Analysis of the ^{13}C and ^{1}H NMR spectra of methoxytetramethylphosphorane (XXX) [41,72] at different temperatures enabled the authors to demonstrate that this compound has a trigonal bipyramidal structure in which the methoxy-group and one of the methyl groups occupy axial positions and the remaining three methyl groups occupy equatorial positions.

IV. CHEMICAL PROPERTIES

1. Thermal Stability

The majority of acyclic penta-alkoxyphosphoranes containing alkyl substituents with the normal structure are liquids which have not been isolated in a pure state. Heating or an attempt to distil them *in vacuo* lead to decomposition. [51,52,54,57] Penta-alkoxyphosphoranes decompose slowly also at room temperature. Thus pentaethoxyphosphorane (XLIII) does not change during storage in a refrigerator for 7 days [57] but decomposes at 20 °C with formation of triethyl phosphate, ethanol, diethyl ether and probably ethylene: [51]

$$\underset{\text{(XLIII)}}{(C_2H_5O)_5P} \xrightarrow{20^\circ C} (C_2H_5O)_3P{=}O + C_2H_5OH + C_2H_5OC_2H_5 + CH_2{=}CH_2\ .$$

Among the penta-alkoxyphosphoranes investigated, pentabenzyloxyphosphorane (LVIII) shows the lowest stability, decomposing fully in the course of two days at room temperature. [57]

The stability of acyclic penta-alkoxyphosphoranes increases somewhat for compounds with branched alkyl substituents. Crystalline pentaneopentyloxyphosphorane (LV), pentacyclopentyloxyphosphorane (LVI), and pentacyclohexyloxyphosphorane (LVII), which are stable for several months at temperatures in the range 0–10 °C, have been isolated in a pure state. [57]

The thermal stability of penta-alkoxyphosphoranes increases to a much greater extent following the enhancement of the electron-accepting properties of the alkyl substituents. Thus pentakis(2,2,2-trifluoro-1-trifluoromethylethoxy)phosphorane (XIV), [29] pentakis(2,2,2-trifluoroethoxy)phosphorane (XV), [27] and pentakis(ααω-trihydropolyfluoroalkoxy)phosphoranes (XVI) and (XVII) [32] distil *in vacuo* without decomposition, while pentakis(2,2,2-trichloroethoxy)phosphorane (XVIII) is a crystalline substance stable on heating to 130 °C in the course of 1 h.[31] All the known penta-aryloxyphosphoranes as well as the alkyl- and aryl-aryloxyphosphoranes (XX), (XXIII)–(XXVI), and (XXIX) are thermally stable, which is apparently also caused by the electron-accepting properties of the aryloxy substituents. In solutions, these phosphoranes are weakly dissociated (the equilibrium constant is less than 10^{-7}):[40,73]

$$(ArO)_5P \rightleftarrows (ArO)_4\overset{+}{P} + ArO^- \ .$$

The replacement of one, two, or three alkoxy-groups by alkyl or aryl-groups as a rule diminishes the thermal stability of the alkoxy-phosphoranes. Thus tributylbis(2,2,2-trifluoroethoxy)phosphoranes (VI) decomposes even at room temperature in 24 h with formation of 20% of bis(2,2,2-trifluoroethyl) ether.[34]

It has been shown by ^1H and ^{31}P NMR [54] that the phosphoranes (XLVI), (XLVII), and (LIII) exist in solutions even at 20 °C in equilibrium with the phosphonium form. The equilibrium has been explained[54] by the fact that the alkyl and aryl substituents at the phosphorus atom stabilise the phosphonium cation:

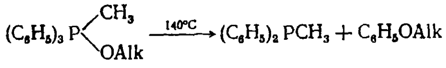
$$R_nP(CH_3)_{3-n}(OC_2H_5)_2 \rightleftarrows R_n\overset{+}{P}(CH_3)_{3-n}(OC_2H_5) + C_2H_5O^-$$
$$R = n\text{-}C_4H_9,\ n = 3\ (XLVI);$$
$$R{=}C_6H_5,\ n = 1\ (LIII),\ n = 0\ (XLVII) \ .$$

The high thermal stability of dimethoxymethyltetramethoxyphosphorane (LV), which does not decompose until 125 °C via a mechanism unusual for acyclic alkoxyphosphoranes (involving the formation of a tervalent phosphorus compound), is noteworthy:[65]

$$(CH_3O)_4PCH(OCH_3)_2 \xrightarrow{\Delta} (CH_3O)_3P + HC(OCH_3)_3 \ .$$
$$(LXV)$$

The thermal stability increases most significantly on passing to phosphoranes containing only one alkoxy-group. The alkoxytetramethylphosphoranes (XXX) and (XXXI) [41] and the alkoxymethyltriphenylphosphoranes (XXXII)–(XXXIV) have been isolated pure by vacuum distillation or crystallisation. They do not decompose until 130–140 °C:[74]

$$(CH_3)_4P(OAlk) \xrightarrow{130°C} (CH_3)_3P{=}O + AlkCH_3$$
$$(XXX),\ (XXXI)$$



$$(C_6H_5)_3P\begin{matrix}\diagup CH_3\\ \diagdown OAlk\end{matrix} \xrightarrow{140°C} (C_6H_5)_2PCH_3 + C_6H_5OAlk$$

(XXXII) — (XXXIV) .

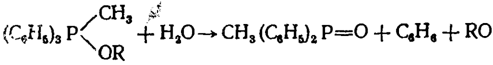
2. Hydrolysis

All the acyclic penta-alkoxy- and penta-aryloxy-phosphoranes as well as alkoxy- or aryloxy-organylphosphoranes, with the exception of $(C_6H_5)_3P[OC(CF_3)_2C_6H_5]_2$ (V),[33] are extremely readily hydrolysed by atmospheric moisture with dissociation of the P–O bond. The hydrolysis of penta-alkoxy- and penta-aryloxy-phosphoranes leads to the formation of alcohols and phenols and phosphates:[9,25,29,32,37,75,76]

$$(RO)_5P + H_2O \rightarrow (RO)_3P{=}O + 2ROH$$
$$R{=}(CF_3)_3CH\ (XIV);\ H(CF_2)_nCH_2,\ n = 2\ (XVI),$$
$$4\ (XVII);\ C_6H_5\ (II);\ CH_3\ (XLIV);\ C_2H_5\ (XLIII) \ .$$

The products of the hydrolysis of the alkoxy- or aryloxyalkyl(aryl)phosphoranes (IV), (XXI), (XLV), (L), and (LII), containing four, three, or two alkoxy-groups, are phosphonates, phosphinates, or tertiary phosphine oxides respectively.[34,38,54,56] The hydrolysis of methoxytetramethylphosphorane (XXX) and the alkoxymethyltriphenylphosphoranes (XXXII)–(XXXIV), containing only one alkoxy-group, proceeds with the dissociation of both P–O and P–C bonds:[41]

$$(CH_3)_4POCH_3 + H_2O \rightarrow (CH_3)_3P{=}O + CH_4 + CH_3OH$$
$$(XXX)$$



$$(C_6H_5)_3P\begin{matrix}\diagup CH_3\\ \diagdown OR\end{matrix} + H_2O \rightarrow CH_3(C_6H_5)_2P{=}O + C_6H_6 + ROH$$

(XXXII)—(XXXIV) .

The P–C bond is ruptured also on hydrolysis of the phosphoranes (VII) (XXXVIII) containing trifluoromethyl groups at the phosphorus atom:[35,50]

$$(CF_3)_3P(OCH_3)_2 + 2H_2O \rightarrow (CF_3)_2PO_2H + CF_3H + 2CH_3OH$$
$$(VII)$$
$$(CF_3)_3P[OSi(CH_3)_3]_2 + H_2O \rightarrow (CF_3)_2PO_2H + CF_3H + [(CH_3)_3Si]_2O \ .$$
$$(XXXVIII)$$

The kinetics and mechanism of the hydrolysis of acyclic alkoxy- and aryloxy-phosphoranes have been investigated[25] in relation to pentaphenoxyphorane (III) and certain substituted penta-aryloxyphosphoranes. The rate of reaction in neutral and alkaline media depends greatly on the electronic and steric properties of the substituents in the aromatic ring (Table 3).

Table 3. The influence of substituents on the rate of hydrolysis of penta-aryloxyphosphoranes at 25 °C in 75% aqueous dimethoxyethane.[25]

Rate constant, s^{-1}	$P(OC_6H_5)_5$	$P(OC_4H_4CH_3\text{-}o)_5$	$P(OC_6H_4CH_3\text{-}n)_5$	$P(OC_6H_4Cl\text{-}o)_5$	$P(OC_6H_4Cl\text{-}n)_5$
k_{H_2O}	0.202	$1.1 \cdot 10^{-5}$	0.0197	0.106	390
k_{H^+}	16.4	1.3	79	—	—
k_{OH^-}	11.4	$7.5 \cdot 10^{-4}$	3.4	—	—

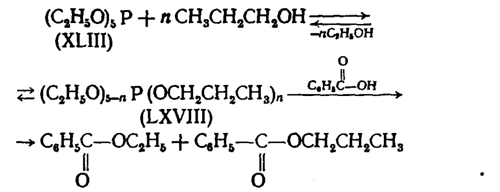
These effects are less pronounced in an acid medium. Kinetic data and especially the appreciable steric effects enabled the authors to suggest that the hydrolysis of pentaphenoxyphosphoranes in neutral and alkaline media also takes place via an intermediate in which the coordination number of phosphorus rises to six:[25]

$$(C_6H_5O)_5P + H_2O \xrightarrow{k_1} (C_6H_5O)_5\overline{P}OH + H^+$$
$$(II)$$
$$(C_6H_5O)_5\overline{P}OH \xrightarrow{k_2} (C_6H_5O)_3P{=}O + C_6H_5OH + C_6H_5O^- \ .$$

The entropies (–188 J mol^{-1} K^{-1}) and enthalpies (22.5 kJ mol^{-1} of activation obtained for the hydrolysis of pentaphenoxyphosphorane (II) in 25% aqueous dioxan also led the authors[75] to the conclusion that this is a multistage process involving the formation of a hexacoordinate intermediate.

3. Reactions with Alcohols

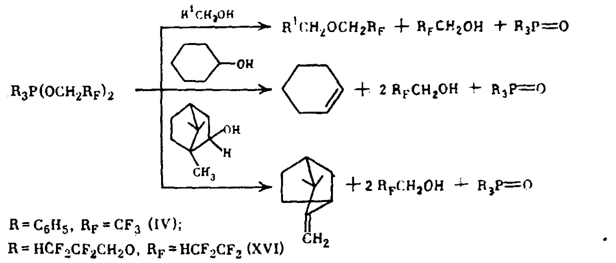
The mode of reaction of alkoxyphosphoranes with alcohols is determined by the nature of the substituents both in the phosphorane and alcohol molecules. In the reaction of pentaethoxy phosphorane (XLIII) with five moles of propyl alcohol, the exchange of ethoxy-groups for propoxy-groups is observed. This apparently results in the formation of the mixed phosphoranes (LXVIII), since treatment of the reaction mixture with benzoic acid entails the formation of ethyl benzoate and propyl benzoate in equal amounts:[76]



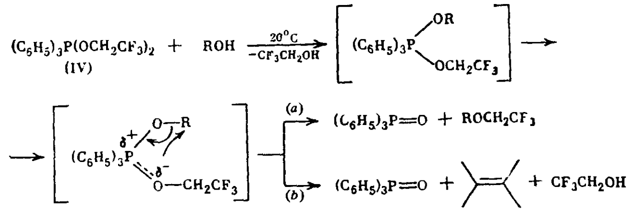
$$(C_2H_5O)_5P + n\,CH_3CH_2CH_2OH \underset{-nC_2H_5OH}{\rightleftarrows} (C_2H_5O)_{5-n}P(OCH_2CH_2CH_3)_n \xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}-OH} C_6H_5\underset{\overset{\|}{O}}{C}-OC_2H_5 + C_6H_5-\underset{\overset{\|}{O}}{C}-OCH_2CH_2CH_3 .$$

(XLIII) (LXVIII)

With enhancement of the electron-accepting properties of the substituents in ethoxyphosphoranes, their tendency to alkylate alcohols also increases. The ethers $ROCH_2P_F$ ($R = C_4H_9$, C_5H_{11}, C_8H_{17}, $C_6H_5CH_2$, or $C_6H_5CH_2CH_2$) are formed when bis(2,2,2-trifluoroethoxy)triphenylphosphorane (IV) [33,34] and pentakis(2,2,3,3-tetrafluoropropoxy)phosphorane (XVI) [69] react with the corresponding primary alcohols. In their reactions with cyclic secondary alcohols (cyclohexanol or borneol), the phosphoranes (IV) and (XVI) exhibit dehydrating properties, as a result of which one observes the preferential formation of olefins:[33,34,69]



2-Phenylethanol interacts with the phosphorane (IV) to form 70% of the ether $C_6H_5CH_2CH_2OCH_2CF_3$ and 11% of styrene:[33,34]



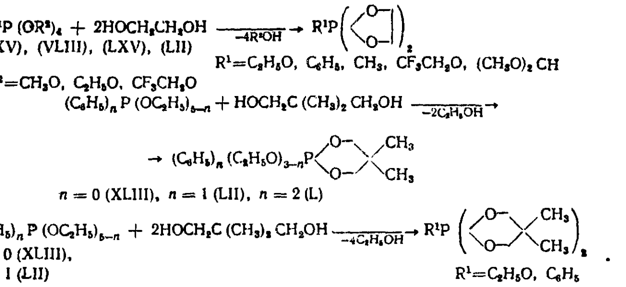
It has been suggested[33,34] that, as a result of attack on the phosphorus atom, one of the trifluoroethoxy-groups is exchanged in the first stage for an alkoxy-group. Then, as a result of nucleophilic attack by the trifluoroethoxide anion on the α-carbon atom of the alkyl group (pathway *a*), ethers are produced. In the cyclic secondary alcohols, the trifluoroethoxide anion apparently attacks the β-carbon atom (pathway *b*), which leads to the formation of olefins.

The possibility of the initial attack by the alkoxide anion on the alkoxyphosphorane molecule precisely at the phosphorus atom has been demonstrated by the formation of compounds of hexacoordinate phosphorus in the reactions of phosphoranes (II), (XI), (XV), (XLIII), (XLIV), and (LXX) with alkoxides or phenoxides:[16,39,69,77]

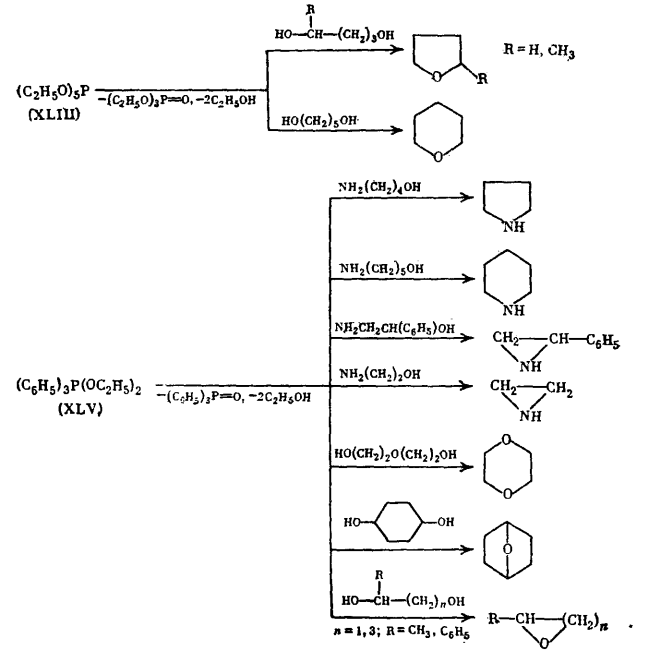
$$(C_6H_5)_nP(OR)_{5-n} + ROM \rightarrow (C_6H_5)_n\bar{P}(OR)_{6-n}\,M^-$$

$n = 0$, $R{=}CH_3$ (XLIV), C_2H_5 (XLIII), C_6H_5 (II), CF_3CH_2 (XV);
$n = 1$, $R{=}CF_3CH_2$ (XI);
$n = 2$, $R{=}CF_3CH_2$ (LXI);
$M^+ = K^+$, Na^+, $(C_2H_5)_3\overset{+}{N}H$.

Acyclic phosphoranes containing at least two alkoxy-groups react with 1,2-glycols to form phosphoranes containing one or two five-membered or six-membered rings.[16,65,69,78] This mode of reaction is apparently associated with the stabilising influence of these rings on the phosphorane structure:[79,80]



The reactions of the alkoxyphosphoranes (XLIII) and (XLV) with diols containing more than three methylene groups and also with aminoalcohols entail the dehydration of the latter and the formation of heterocycles, probably as a result of the decomposition of the intermediate unstable phosphoranes:[78,81-83]



Reactions are rapid at room temperature and can serve as a convenient preparative method for the synthesis of simple heterocycles.

4. Reactions with Phenols

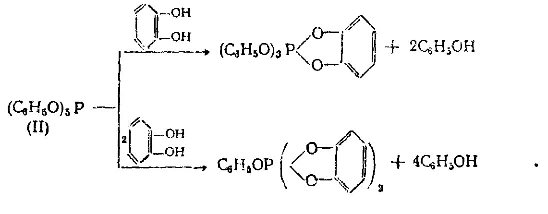
Pentamethoxy- and pentaethoxy-phosphoranes (XLIV) and (XLLIII) react with various phenols at room temperature, as a result of which phenol ethers are formed in high yields:[76,84]

$$(RO)_5P + ArOH \rightarrow (RO)_3P{=}O + ArOR + ROH$$

$R{=}CH_3$ (XLIV), C_2H_5 (XLIII)

Pentakis(polyfluoroalkoxy)phosphoranes (XVI) and (XVII) interact with phenols only at 150–160 °C, but phenol alkylation products are not then formed. According to ^{31}P NMR data, when equimolar amounts of the phosphorane (XVII) and phenol are heated, nucleophilic substitution of the polyfluoroalkoxy-group by the phenoxy-group takes place and an equilibrium mixture of the initial phosphorane (XVII) and a mixed phenoxytetrakis(polyfluoroalkoxy)phosphorane is formed.[59]

In the reaction of pentaphenoxyphosphorane (II) with catechol, the phenoxy-groups are substituted and cyclic phosphoranes are formed:[85]

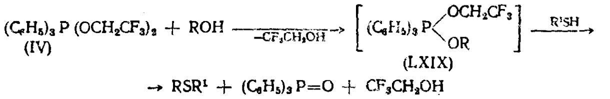


5. Reactions with Thiophenols and Mercaptans

Acyclic alkoxyphosphoranes alkylate thiophenols and mercaptans at room temperature. The product of the alkylation of thiophenol by pentamethoxyphosphorane (XLIV), namely methyl phenyl sulphide, is formed in 90% yield:[84]

$$\underset{\text{(XLIV)}}{(CH_3O)_5P} + C_6H_5SH \rightarrow C_6H_5SCH_3 + (CH_3O)_3P{=}O + CH_3OH$$

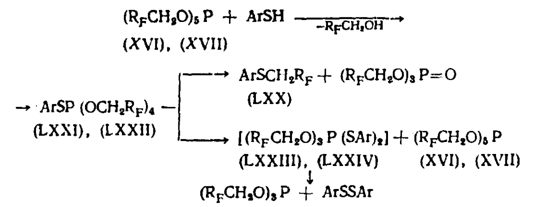
The alkoxy(2,2,2-trifluoroethoxy)triphenylphosphoranes (LXIX), formed as intermediates in the reactions of the phosphorane (IV) with alcohols, are also convenient alkylating agents for thiophenols and mercaptans:[34,86]



$$\underset{\text{(IV)}}{(C_6H_5)_3P(OCH_2CF_3)_2} + ROH \xrightarrow[-CF_3CH_2OH]{} \underset{\text{(LXIX)}}{\left[(C_6H_5)_3P\begin{smallmatrix}OCH_2CF_3\\ OR\end{smallmatrix}\right]} \xrightarrow{R^1SH} RSR^1 + (C_6H_5)_3P{=}O + CF_3CH_2OH$$

$R{=}C_2H_5$, $CH_3CH_2CH_2$, $C_6H_5CH_2$,
$C_6H_5CH_2CH_2$, *cis*-$CH_3CH{=}CH{-}CH_2$,
trans-$CH_3CH{=}CHCH_2$ $CH_2{=}CHCH(CH_3)$,
trans-$C_6H_5CH{=}CHCH_2$;
$R^1{=}C_6H_5$, $C_6H_5CH_2$, $CH_3(CH_2)_3$, C_2H_5 .

In contrast to compound (IV), pentakis(polyfluoroalkoxy)phosphoranes (XVI) and (XVII) react with thiophenols only on heating. The yields of the alkylation products, i.e. aryl polyfluoroalkyl sulphides (LXX), then diminish with increase of the length of the polyfluoroalkyl chain.[17] The reactions of the phosphoranes (XVI) and (XVII) with thiophenols take place as a result of the initial attack by the thiophenol on the phosphorus atom with formation of arylthiotetrakis(polyfluoroalkoxy)phosphoranes (LXXI) and (LXXII).[17] The way subsequent reactions take place depends on the length of the polyfluoroalkyl chain of the substituent.

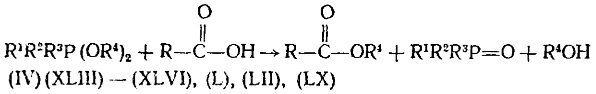


$R_F{=}HCF_2CF_2$ (XVI), (LXXI), (LXXIII)
$R_F{=}H(CF_2CF_2)_2$ (XVII), (LXXII), (LXXIV) .

The arylthiophosphorane (LXXI) is largely converted into the sulphide (LXX) and phosphate via the mechanism of the second stage of the Arbuzov reaction and disproportionates to the phosphoranes (XVI) and (LXXIII) only to a slight extent. However, the arylthiophosphorane (LXXII) is to a considerable extent converted into the di(arylthio)phosphorane (LXXIV) together with decomposition via the mechanism of the Arbuzov rearrangement. Compound (LXXIV) is unstable and decomposes under the reaction conditions to a phosphite and a disulphide, which has been confirmed by a special experiment.[17,69]

Reactions with Acids

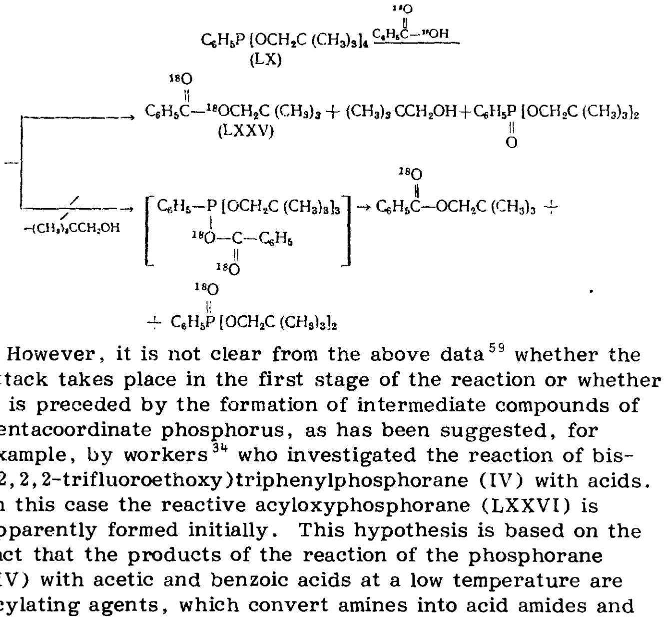
Acyclic alkoxyphosphoranes react vigorously with carboxylic acids at room temperature to form products of the alkylation of the latter—esters:[33,34,53,54,59,76,84]



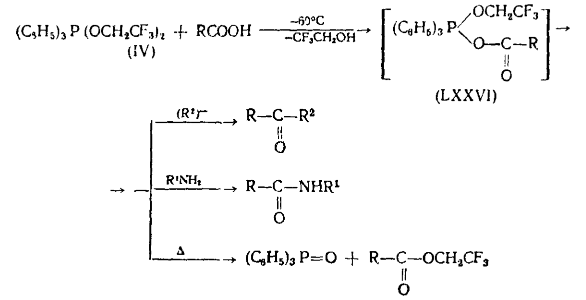
$$R^1R^2R^3P(OR^4)_2 + R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \rightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR^4 + R^1R^2R^3P{=}O + R^4OH$$

(IV)(XLIII) – (XLVI), (L), (LII), (LX)

It has been shown[59] that in the reaction of tetraneopentylphenylphosphorane (LX) with [^{18}O]-labelled benzoic acid, both isotopic ^{18}O atoms are located in the molecule of the ester (LXXV), i.e. the acid attackes the α-carbon atom of the alkoxy-substituent:



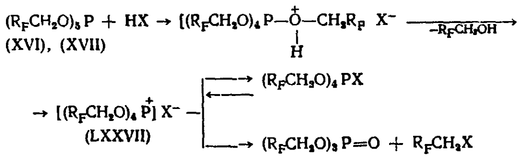
However, it is not clear from the above data[59] whether the attack takes place in the first stage of the reaction or whether it is preceded by the formation of intermediate compounds of pentacoordinate phosphorus, as has been suggested, for example, by workers[34] who investigated the reaction of bis(2,2,2-trifluoroethoxy)triphenylphosphorane (IV) with acids. In this case the reactive acyloxyphosphorane (LXXVI) is apparently formed initially. This hypothesis is based on the fact that the products of the reaction of the phosphorane (IV) with acetic and benzoic acids at a low temperature are acylating agents, which convert amines into acid amides and alkyl or aryl anions into ketones:[34]



$R{=}CH_3$, C_6H_5
R^1, $R^2{=}$Alk, C_6H_5 .

On the other hand pentakis(polyfluoroalkoxy)phosphoranes (XVI) and (XVII) do not react with acetic and benzoic acids on heating to 100 °C in the course of 4 h. 2,2,3,3-Tetrafluoropropyl benzoate is formed only after prolonged heating of the reactants at 170 °C.[69]

Bearing in mind the ability of the oxygen atom in alkoxyphosphoranes to be protonated by acids,[87,88] one may put forward a general mechanism of the reactions of acyclic alkoxyphosphoranes with acids, consisting in the protonation of oxygen and subsequent splitting off of the alcohol and the formation of the phosphonium salt (LXXVII), which may exist in equilibrium with the acyloxyphosphorane. The decomposition of the salt (LXXVII) actually leads to the final reaction products:

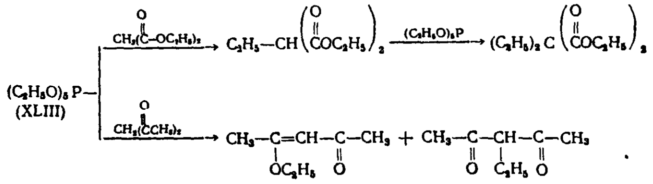


$R_F=H(CF_2)_n$, $n=2$ (XVI), 4 (XVII);
$X^-=C_6H_5COO^-$, Cl^- .

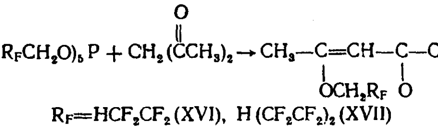
Evidently the difference between the reactivities of the alkoxyphosphoranes (IV), (XLIII), (XLVII), (L), (LII), and (LX) and of the polyfluoroalkoxyphosphoranes (XVI) and (XVII) in relation to acids is associated with the influence of the polyfluoroalkyl substituents, which weakens the nucleophilic properties of the oxygen, hindering its protonation.

7. Reactions with CH Acids

Pentaethoxyphosphorane (XLII) ethylates diethylmalonic ester at the carbon atom and acetylacetone at the oxygen atom. An insignificant amount of the *C*-alkylation product is also formed in the latter case:[76]



Pentakis(polyfluoroalkoxy)phosphoranes (XVI) and (XVII) react with acetylacetone to form vinyl ethers only:[89]

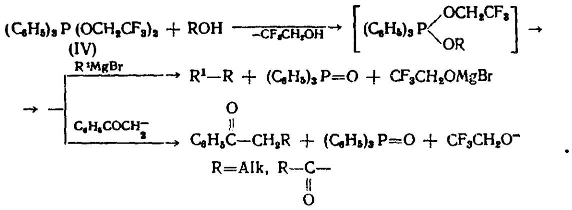


$$(R_FCH_2O)_5P + CH_2(\overset{O}{\overset{\|}{C}}CH_3)_2 \rightarrow CH_3-\underset{OCH_2R_F}{\underset{|}{C}}=CH-\underset{O}{\underset{\|}{C}}-CH_3$$

$R_F=HCF_2CF_2$ (XVI), $H(CF_2CF_2)_2$ (XVII) .

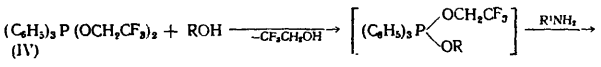
8. Reactions with Carbanions

Succesive treatment of bis(2,2,2-trifluoroethoxy)triphenylphosphorane (IV) with an alcohol or acid and then with a Grignard reagent or the enolate anion results in the formation of compounds with a C–C bond—alkanes or ketones. It is believed[34] that the carbanion executes a nucleophilic attack on the intermediate highly reactive alkoxy- or acyloxy-phosphorane:



9. Reactions with Amines and Carboxylic Acid Amides

The structure of the products of the reactions of alkoxyphosphoranes with primary amines is determined by the nature of the substituents at the phosphorus atom. When bis(2,2,2-trifluoroethoxy)triphenylphosphorane (IV) is treated with an alcohol and then a primary amine, the latter is alkylated and a secondary amine is formed:[34]

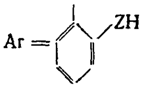


$\rightarrow RR^1NH + CF_3CH_2OH + (C_6H_5)_3P{=}O$

$R = n\text{-}C_8H_{17}$, $C_6H_5CH(CH_3)$, $C_6H_5CH_2$,
trans-$CH_3CH{=}CHCH_2$, $CH_2{=}CHCH(CH_3)$;
$R^1{=}CH_3(CH_2)_3$, $CH_3(CH_2)_2$, C_6H_5 .

Primary arylamines are alkylated also in the reaction with bis(2,2,2-trifluoro-1-trifluoromethylethoxy)triphenylphosphorane (LXXVIII):[90]

$$\underset{\text{(LXXVIII)}}{(C_6H_5)_3P[OCH(CF_3)_2]_2} + ArNH_2 \rightarrow \underset{\text{(LXXIX)}}{ArNH-CH(CF_3)_2} + HOCH(CF_3)_2 + (C_6H_5)_3P{=}O$$



Ar = ; Z=O, S, NH .

The secondary amines (LXXIX) thus produced have been used successfully for the synthesis of heterocyclic systems.[90]

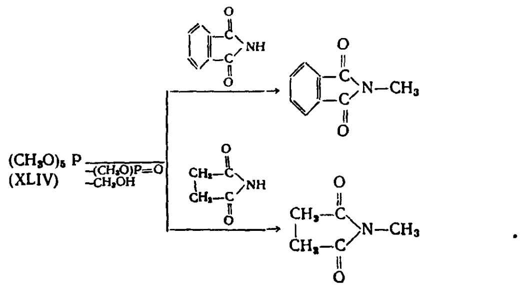
In contrast to the examples quoted above, the reactions of pentakis(polyfluoroalkoxy)phosphoranes (XVI) and (XVII) with primary arylamines lead to tris(polyfluoroalkoxy)phosphazobenzenes (LXXX):[69]

$$[H(CF_2)_nCH_2O]_5P + ArNH_2 \rightarrow \underset{\text{(LXXX)}}{[H(CF_2)_nCH_2O]_3P{=}NAr} + 2H(CF_2)_nCH_2OH$$

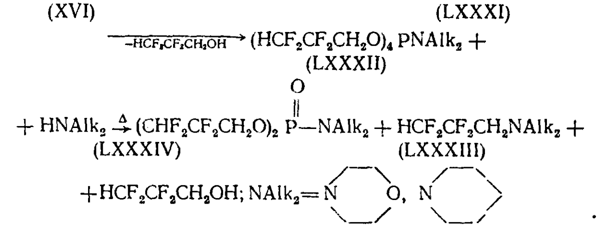
$n=2$ (XVI), 4 (XVII) .

There are very few data on the reactions of acyclic alkoxyphosphoranes with compounds containing a secondary aminogroup.

Pentamethoxyphosphorane (LXIV) reacts with phthalimide and succinimide to form *N*-methylated compounds:[84]



Detailed study of the reaction of pentakis(2,2,3,3-tetrafluoropropoxy)phosphorane (XVI) with secondary amines[91] showed that a compound of hexacoordinate phosphorus with an acyclic structure, namely dialkylammonium pentakis(2,2,3,3-tetrafluoropropoxy)piperidino(morpholino)phosphorate (LXXXI), is formed initially even at 20 °C as a result of the attack by the amine on the phosphorus atom. The phosphorates (LXXXI) are crystalline compounds stable at 20 °C. When they are heated to 150 °C, the nucleophilic substitution of the 2,2,3,3-tetrafluoropropoxy-group takes place and the mixed piperidino(morpholino)tetrakis(2,2,3,3-tetrafluoropropoxy)phosphorane (LXXXII) is produced. The latter alkylates a second amine molecule and the final products of the reaction of the phosphorane (XVI) with piperidine or morpholine on heating are therefore the tertiary amine (LXXXIII), the phosphoramidate (LXXXIV), and tetrafluoropropanol:



$$\underset{\text{(XVI)}}{(HCF_2CF_2CH_2O)_5P} + 2Alk_2NH \xrightarrow{20^\circ C} \underset{\text{(LXXXI)}}{(HCF_2CF_3CH_2O)_5\,\bar{P}NAlk_2H_2\overset{+}{N}Alk_2} \xrightarrow{\Delta}$$

$$\xrightarrow[-HCF_2CF_2CH_2OH]{} \underset{\text{(LXXXII)}}{(HCF_2CF_2CH_2O)_4PNAlk_2} +$$

$$+ HNAlk_2 \xrightarrow{\Delta} \underset{\text{(LXXXIV)}}{(CHF_2CF_2CH_2O)_2\overset{O}{\overset{\|}{P}}{-}NAlk_2} + \underset{\text{(LXXXIII)}}{HCF_2CF_2CH_2NAlk_2} +$$

$$+ HCF_2CF_2CH_2OH;\ NAlk_2 =$$

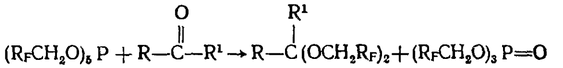
10. Reactions with Aldehydes and Ketones

Bis(2,2,2-trifluoroethoxy)triphenylphosphorane (IV) reacts with aliphatic aldehydes at room temperature to form bis(2,2,2-trifluoroethyl)acetals:[31]

$$\underset{\text{(IV)}}{(C_6H_5)_3P(OCH_2CF_3)_2} + RCHO \rightarrow (C_6H_5)_3P{=}O + RCH(OCH_2CF_3)_2$$

$$R{=}(CH_3)_2CH,\ n\text{-}C_5H_{11},\ n\text{-}C_6H_{13}.$$

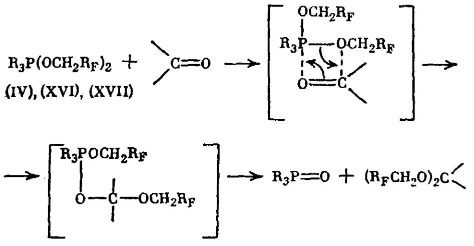
Pentakis(polyfluoroalkoxy)phosphoranes (XVI) and (XVII) alkylate on heating formaldehyde and also aldehydes and ketones with electron-accepting substituents but do not react with the usual aliphatic aldehydes and ketones even at 200 °C:[89]



$$(R_FCH_2O)_5P + R{-}\overset{O}{\overset{\|}{C}}{-}R^1 \rightarrow R{-}\overset{R^1}{\overset{|}{C}}(OCH_2R_F)_2 + (R_FCH_2O)_3P{=}O$$

$$R_F{=}HCF_2CF_2\ \text{(XVI)},$$
$$H(CF_2CF_2)_2\ \text{(XVII)}$$
$$R{=}R^1{=}H;\ R{=}Ar,\ R^1{=}H;\ R{=}C_6H_5CH{=}CH,\ R^1{=}H;$$
$$R{=}CH_3CH{=}CH,\ R^1{=}H;\ R{=}R^1{=}CF_3.$$

It has been suggested[34,89] that the alkylation proceeds via a four-membered cyclic transition state, which is produced as a result of the initial attack by the positively charged carbon atom of the carbonyl group on the oxygen atom of the polyfluoroalkoxyphosphorane:



$R = C_6H_5$, $R_F = CF_3$ (IV); $R = H(CF_2CF_2)_nCH_2O$, $R_F = H(CF_2CF_2)_n$, $n = 1$ (XVI), $n = 2$ (XVII)

The significant difference between the reactivities of the phosphorane (IV), on the one hand, and the phosphoranes (XVI) and (XVII), on the other, can apparently be explained by the weakening of the nucleophilic properties of the oxygen of the polyfluoroalkoxy-group in the molecules of compounds (XVI) and (XVII), as a result of which the attack on the carbon atom of the carbonyl group is possible only after an increase of the positive charge on the latter.

The literature data examined show that the methods of synthesis of derivatives of acyclic hydroxyphosphoranes known at present make it possible to obtain compounds containing substituents with different electronic and steric properties at the phosphorus atom; this alters in its turn their chemical properties within extremely wide limits.

Acyclic alkoxyphosphoranes are extremely reactive reagents, suitable for the synthesis of various classes of organic compounds. Special mention should be made of the advantages of alkoxyphosphoranes as alkylating agents: the alkylation takes place under mild conditions in the absence of basic or acid catalysts and does not require the use of protecting groups; the reaction does not result in the formation of acids or bases, which are in many instances undesirable.

Since vigorous investigation of the chemical properties of acyclic alkoxyphosphoranes began only recently, many reactions have been examined in relation to a limited number of examples. There is no doubt that further study of acyclic alkoxy- and aryloxy-phosphoranes will greatly expand the range of synthetic applications of these reactive compounds and will also lead to the discovery of new facts, which will extend our understanding of the nature of phosphorus compounds.

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Modern Chemical Physics. Aims and Pathways to Progress

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I. CHEMICAL PHYSICS IN MODERN CHEMISTRY

Modern chemistry has become a high risk science. Progress in engineering and technology requires from chemistry the creation of new substances and materials with extreme and frequently contradictory and at first sight incompatible properties, the development of economical efficient technologies based on new non-traditional principles, the creation of new means for the control and diagnostics of processes and materials, and the development of new principles of chemical energetics. Under these conditions, scientific research along traditional lines of trial and error has become very refined, laborious, and expensive and the risk of unsuccessful research, the risk of invalid trials, and the risk of errors have increased. The more complex the problem, the greater the risk of failure and of fruitless expenditure of labour, materials, and time.

The degree of risk can be reduced only on the basis of a profound knowledge of the physics of chemical processes, the theory of structure, molecular organisation, the functioning and transformation of chemical systems, and a profound analysis of the predictions following from such knowledge and understanding, i.e. on the basis of the principles constituting chemical physics. The level of this science and its state determine the horizons of chemical materials science, chemical synthesis, chemical technology and power generation, chemical diagnostics, and environmental chemistry. Naturally, each of these fields develops as a result of its intrinsic internal potential frequently entirely without being based (or not knowingly based) on chemical physics, but the increase of the complexity of chemical problems, which can be seen objectively to arise from scientific and technical progress, inevitably makes it necessary to resort to chemical physics, its corollaries and predictions, and its growing predictive power.

The aim of this article is to analyse the concerns of modern chemical physics, its present level, its aims, its ability to reduce the risks discussed above, and its growing points and prospects.

II. STRUCTURE OF MATTER

The atomic-molecular and electronic structures of chemical species and substances constitute the classical problem of chemical physics. Structure is the first, key element in the series structure–property–function. The determination of relations in this series is a problem of fundamental importance; its solution makes it possible to predict on the basis of the structure of the substance its function and purpose and its likely usefulness and applications.

Traditionally chemical physics has been concerned with the direct problem—the determination of structure and then the investigation of properties, which resulted in the determination of the field in which the given substance can be used and can function. However, the converse problem has become increasingly acute in modern chemistry—the creation of chemical structures with a specified atomic-molecular architecture in order to ensure specified properties and functions of these structures. This is important in the creation of purpose-designed drugs, semiconducting materials with specified conducting properties, alloys with specified corrosion resistance, ceramic materials with definite thermal and mechanical stabilities, optical glasses with specified electrochromism, etc.—the generality of this problem is universal.

This Section deals with the level and style in which modern chemical physics solves structural problems and the characteristics, trends, methods, and means used in such solutions. They are different for structures with different scales and levels of organisation and we shall therefore immediately introduce the following classification: isolated species (atom, molecule, ion, and radical), small assemblies (van der Waals molecule, complex, macromolecule, micelle, cluster), and large assemblies (crystal, liquid, amorphous body, membrane, etc.).

1. Isolated Species

The determination of the structural-chemical and structural-physical parameters of isolated species is the traditional task of chemical physics; these parameters characterise the electron shell and nuclear skeleton of the species (the angles and distances between atoms and bonds, the frequencies and amplitudes of vibrations, internal rotations, inversions, and conformational transitions, the energies and symmetries of the electronic, vibrational, and rotational states, ionisation potentials, electron affinities and bond energies, the polarisability tensor, the magnetic and electrical dipole moments, the charge and spin distributions, the dipole moments of electronic transitions, the oscillator strengths, the electron delocalisation frequencies, the energies of quadrupole and electron-nucleus magnetic interactions, etc.). They are required for calculations on the thermodynamics of gases and plasma, for the calculation of the composition of species and their state, for the prediction of properties, stability, and conditions governing the existence and the reactions of chemical systems (especially at high and ultrahigh temperatures). They are needed in chemical energetics (emissive power of high-temperature gases under non-equilibrium conditions, the functioning of gas lasers, etc.).

Three new features have imparted a modern "aspect" to this traditional task of chemical physics: intense efforts to attain highly excited states, the endeavour to characterise "exotic" species, and finally, the very high (sometimes close to the limit) metrological accuracy.

The very marked tendency to specify the structural and spectroscopic characteristics of excited states—just as complete as for the ground state—has arisen for a number of reasons. Firstly, this is associated with the search for new laser systems and the choice of species (emitters) suitable for generation. For this purpose, one needs knowledge of the spectroscopy of the species which is as complete as possible—the energy and symmetry of the excited levels, the radiative lifetimes, the probabilities of the radiative and non-radiative transitions, etc.

Secondly, it is needed as an analytical means for the identification and recognition of excited species in processes induced by electron impact, photo-excitation, and powerful collisions (the chemistry and optics of the atmosphere, space chemistry and plasma, high-temperature chemistry, combustion and explosion, shock waves, etc.).

Thirdly, the properties of excited states and their potential energy surfaces are needed for the prediction of reaction pathways, for the prediction of orbital symmetry-dependent prohibitions, for the assessment of the adiabatic nature of reactions and calculations on the chemical dynamics of elementary processes, for the analysis of ways of transforming chemical energy and procedures for the chemical pumping of the reaction products. An enormous amount of work has already been carried out on the characteristics of the excited state of atoms and diatomic and triatomic molecules and radicals and this "energy programme" in chemical physics has been extended increasingly to polyatomic molecules and radicals; the principal research techniques are laser and microwave spectroscopy in different versions and combinations. The "energy programme" in chemical physics is characterised most strikingly by the enormous range of the states of atoms investigated—from hot, Rydberg atoms to ultracold atoms.

When the valence electron is excited to high orbitals with large values of the principal quantum number n (n reaches values of several tens up to 100) and is remote from the nucleus, its energy levels are described by the familiar simple Rydberg formula and such excited atoms are referred to as Rydberg atoms. The energy transitions between levels with high values of n correspond to millimetre waves; the energy of the levels is altered by an external electric field, which can even induce the ionisation of the Rydberg atoms; one method for their detection is based on this phenomenon.

The properties and energetics of Rydberg atoms have been investigated quite widely and in fair detail. For example, even the isotopic shifts in the energy of the atoms, caused by the magnetic electron–nucleus interaction, have been measured. Thus the difference between the energies of the ^{86}Sr (nuclear spin $I = 0$) and ^{87}Sr ($I = 9/2$) isotopes and its dependence on n have been measured for the Sr ($5sns$) atoms. The difference ΔE is 0.4 GHz for $n = 35$, 0.9 GHz for $n = 50$, and 1.7 GHz for $n = 70$; in the limit at $n \to \infty$, ΔE tends to 2.8 GHz—the energy of the hyperfine interaction of the 5s electron with the ^{87}Sr nucleus.

One of the remarkable properties of Rydberg atoms is as follows. In a resonator with a very high Q-factor, the photon emitted by a Rydberg atom is retained for a fairly long time, so that it can be recaptured by the same atom. Hence arises the possibility of constructing a single-atom laser, in which a two-level atom interacts with a single-frequency electromagnetic field, which is accompanied by the absorption and emission of the same photon by the same atom. A system which will make it possible to test experimentally the postulates and predictions of quantum electrodynamics is being created at the present time. From this point, chemical physics is at the junction with atomic physics and quantum electrodynamics.

The preparation of ultracold atoms is based on the alteration of the velocity of an atom following the absorption of an optical quantum (laser cooling of atoms). If the atoms and laser photons are tuned in such a way that the absorption takes place in the low-frequency wing of the absorption line, then the resonance absorption by the atom moving towards the photons shifts to the centre of the line and intensifies by virtue of the Doppler shift, whereas for atoms moving in the same direction as the stream of photons the Doppler effect displaces the resonance from the centre of the line and decreases the absorption. As a result the atoms experience a retarding force directed along the stream of photons. If the atoms are now placed in opposed laser beams directed along three orthogonal axes, it is possible to ensure a comprehensive retardation of the atoms. In such a laser field, the movement of the atoms is retarded with a velocity decay time of $\sim 10^{-4}$ s as if they were in an optically viscous medium, which is referred to as "optical treacle". Thus Na atoms can be cooled to 2.4×10^{-4} K and in principle there is a possibility of cooling down to 10^{-6}–10^{-10} K.

Ultracold atoms, virtually lacking kinetic energy, are of interest in precision spectroscopy and in the probing of atom–atom and atom–surface potentials. They also lead to a unique possibility of an experimental test of the fundamental postulates of quantum mechanics, in particular of Bose condensation. Here again, chemical physics adjoins quantum physics.

The second feature of modern structural chemical physics involves a sharp and bold expansion of the assortment of species investigated, including the chemical bonds between the atoms of the elements of almost the entire Periodic System in various combinations, many of which were not so long ago regarded as exotic: Si_2H_2, AsH_2, AsN, CrO^+, PH, ZrO, BeTi, LiPd, Cd_2, CsH, BI, SeO^+, PCl^+, NaCr, HCr, ScLi, SrBr, Si_3, Si_2C, SeS, Li_3, MgC_2, CrN^+, CrC^+, muonium and muonium-containing molecules, ions, and radicals, etc.—the list of such species is becoming ever longer. The distances and angles between atoms, the vibration frequencies, the energies of the ground and excited states, the Coriolis constants, the spin-rotational and spin–spin interactions, potentials, etc. have been measured for them. These trends have been stimulated by the search for new laser systems, the research into the spectroscopic detection of high-energy processes in plasma, in flames, in interstellar space, and in the atmospheres of the stars and planets, and also the search for ways of synthesising new substances and materials. Earlier such exotic molecules were detected predominantly in space, whilst nowadays they are obtained and investigated in wide assortment under laboratory conditions.

The third feature is the extremely high metrological level of the structural information and its exact quantitative description, i.e. the high level of what can be designated in English by the simple word quantification (the corresponding Russian term "kolichestvennost'" is unusual and is hardly likely to be adopted in our language). Thus the hyperfine interaction energy in the Cs atom in the ground $^2S_{1/2}$ state is 9192631784 ± 31 Hz and has been measured with an accuracy of 1 part in 10^9. Furthermore, the dependence of this quantity a on the inert gas pressure p has been measured; the change amounts to approximately 10^{-6} of a. For He and Ne, $da/dp = +874$ and 450.2 Hz GPa^{-1}, while for Ar we have $da/dp = -146.7$ Hz GPa^{-1}, which means that the collisions of the Cs atom with He and Ne "clamp" the unpaired Cs electron to the nucleus and intensify the electron–nucleus interaction, while collisions with Ar move the electron away from the Cs nucleus and diminish this energy (probably as a result of the mutual "adhesion" of the Cs and Ar atoms and the partial, approximately 10^{-6}, electron transfer from Cs to Ar). In the excited state $^2P_{1/2}$, the hyperfine interaction energy is 1168 MHz, while in the $^2P_{3/2}$ state it is only 200 MHz. The latter values were obtained with coherent laser excitation of the D_1 and D_2 lines of the Cs atoms and from the observed quantum beats in the transitions between the levels of the hyperfine structure.

The molecular constants of MgO, PbO, and N_2O_3 have been measured with a high degree of accuracy for all the isotopic forms of these molecules and the quadrupole and magnetic interaction tensors and the spin-rotational coupling constants have been determined. The molecular constants for all the isotopic forms of O_2 [including the constants of the magnetic spin-Hamiltonian and among these the constant for the hyperfine interaction with the ^{17}O nucleus: $a(^{17}O) = -54.758$ MHz] have been determined. Measurements have been made with a high degree of accuracy for the hyperfine interactions (both isotropic and anisotropic) of the radical-cation $Cr(CO)_4^+$ with the ^{53}Cr and ^{13}C nuclei and on their basis it was concluded that the above radical-cation has the T_d symmetry and that the unpaired electron is localised in the pure σ orbital. These are only a few instances demonstrating how the high metrological level of the structural information ensures the reliability and non-ambiguity of the conclusions concerning the chemical structure of the species.

The high degree of "quantification" of structural chemical physics reflects, on the one hand, the high metrological level of the modern physical research methods—magnetic resonance in its different versions, Mössbauer, microwave, laser, X-ray, and photoelectron spectroscopy, mass spectrometry, and their numerous "hybrid" combinations. On the other hand, it is of practical value for quantum magnetometry with its frequency standards—it ensures the "raising" of the accuracy and reliability of quantum chemistry as well as the improvement of its computational methods and schemes.

2. Small Assemblies

Small assemblies occupy a position intermediate between individual molecules and continuous systems constituting a phase (liquid, crystal, amorphous glass, etc.). They represent a bridge between the individual molecules and their infinitely large assembly, where intermolecular interactions arise and the characteristics of matter are manifested.

Depending on the character and strength of the intermolecular interactions in the substance, either the properties and features of individual molecules are retained or they are completely lost.

In chemical physics there is an old problem which has now got, as it were, a new lease of life by virtue of advances in the study of the structure and properties of small assemblies. This is the problem of how the hierarchy based on composition (ranging from an individual molecule to a substance) is related to the hierarchy based on properties and functions in a given series, for which quantitative compositions are the qualitative features of a substance (or a phase) manifested, and for what number of individual species does the combined assembly of the latter become a substance and does this occur gradually or is there a "critical" threshold mass.

Van Der Waals Molecules and Complexes. The term van der Waals molecules is given to weakly bound complexes of atoms, radicals, or molecules which exist by virtue of intermolecular attraction. They are observed in rarefied molecular beams, gas streams expanding at ultrasonic velocities, in solid inert gas matrices, and in liquids, and are investigated by laser and microwave spectroscopic methods. An enormous number of such species are known: He_2, Xe_2, $(H_2)_2$, Hd.Ar, $(HF)_2$, Hg.He, $C_6H_6.CH_4$, ICl.Ne, HF.CO, $(N_2O)_2$, $(CO_2)_2$, $(SF_6)_2$, $OCS.CH_4$, Mg.Ca, $H_2S.Ar$, $C_2H_4.Ar$, $C_2H_4.NO$, CO.He, HCl.Xe, $(C_2H_2)_2$, etc. The completeness, reliability, and "quantification" of the structural information for such molecules and complexes is not inferior to that for isolated species. For van der Waals molecules, measurements are made of the symmetry and geometry (on the basis of the rotational spectra and moments of inertia), the quadrupole and spin–spin interaction constants, the rotational g-factors, the magnetic susceptibility and its anisotropy, the dipole and quadrupole moments, the vibration frequencies, the dissociation energies, the lifetimes, etc.

Thus $HCl.C_2H_4$ and $HCl.C_2H_2$ have the T-form: the axis of HCl passes through the centre of the partner molecule and is perpendicular to its axis. The distance from the Cl atom (it is the more remote) to the centre of the partner molecule is 3.724 and 3.699 Å for C_2H_4 and C_2H_2 respectively. In the van der Waals molecules $HCl.C_3H_6$ and $HCl.C_6H_6$, the HCl axis is perpendicular to the planes of the cyclopropane and benzene molecules and coincides with the C_{3v} and C_{6v} symmetry axes of these molecules. The distances from the remote Cl atom to the C_3H_6 and C_6H_6 planes are 3.567 and 3.629 Å. The molecules Kr.HCl and Kr.DCl are linear and their dissociation energies are 179 and 200 cm^{-1}, i.e. even a negligible isotope effect in the dissociation energies is readily measurable. The partner molecules CO and HF are organised into a linear complex with $C_{\infty v}$ symmetry, in which the H atom is "stuck" to the C atom; the dipole moment of the complex, measured on the basis of the Stark effect in the ground vibrational state for the rotational transition $J = 1 \rightarrow 2$, amounts to 2.352 D. The complex of N_2 with HF is linear, i.e. N(1)–N(2).HF; for this complex, the components of the quadrupole interaction tensor involving both ^{14}N nuclei have been measured and it has been found that the addition of the HF molecule induces a shift of electron density from N(1) to N(2), amounting to 0.03 of an electron.

In the NaK molecules, the partners are held together by long-range van der Waals forces and the two electronic states differing in spin ($^1\Sigma^+$ and $^3\Sigma^+$) are therefore energetically equivalent with a dissociation energy $D_e = 203.1$ cm^{-1} and an interatomic distance of 5.457 Å. For NaLi($X^1\Sigma^+$), we have $D_e = 6850$ cm^{-1} and in the excited state ($B^1\Pi$) the corresponding value is $D_e = 1758$ cm^{-1}. In the LiLi, LiNa, LiK, LiRb, and LiCs series, the vibration frequency decreases linearly from 350 to 180 cm^{-1} as a function of $m^{1/2}$, where m is the reduced mass of these van der Waals molecules (these results have been obtained in molecular beams using the laser-induced fluorescence of these molecules).

The dynamics of the van der Waals molecules, namely the lifetime in the ground state, the lifetimes in the excited and dissociative states, the distribution of the energy among the fragments after dissociation, etc., has been studied in detail. Thus the $He.I_2$ molecule exists for ~100 ps, while the lifetime of $H_2.Ar$ is three times longer; in both cases τ decreases with increase of the excess energy. The energetics and "energy problems" of the van der Waals molecules are examined in greater detail in Section IV.

In a liquid, the shifts of the lines in the electronic absorption spectra and their dependence on the polarisability of the solvents are believed to indicate the presence of van der Waals molecules. Thus the combination of the partner molecules in the species $C_6H_6.He$, $C_6H_6.Ar$, $C_6H_6.CH_4$, CH_4.toluene, CH_4.aniline, Ar.toluene, etc. has been identified.

The question arises why there is so much interest in the van der Waals molecules and why they are needed. The van der Waals molecules are the most reliable and the richest source of information about the intermolecular atom–atom pair potentials—their form and parameters; by virtue of these molecules, intermolecular potentials have now entered the age of high spectroscopic accuracy. Furthermore, a reduced potential has been found for inert gas atom pairs which is universal for these pairs and describes the interaction of the atoms with an accuracy better than to within 1%. One of the important questions is whether this universality is a common property of any pairs of atoms or whether it applies only to pairs of inert gas atoms and this question still awaits an answer.

Intermolecular potentials are reference quantities in problems of molecular dynamics in liquids, glasses, and macromolecules, in problems of chemical dynamics (calculation of the trajectories traversed by the reacting systems on the potential energy surface), in problems concerning intermolecular energy transfer and energy relaxation (in this case the efficiency of the transfer or relaxation is determined by the Fourier component of the potential and the frequency of the energy transition).

Interatomic and intramolecular potentials are responsible for the molecular organisation of crystals and large molecules, the packing of molecules in liquids, glasses, etc. A high accuracy of the potentials over all distances is required for such purposes and potentials of different interactions are needed: atom–atom, atom–non-spherical molecule, molecule–molecule, molecule–ion, etc.

The formation of van der Waals molecules is manifested in the macroscopic properties of gases—it alters the form of the pVT diagrams, the second virial coefficient, and the viscosity. These molecules induce the condensation of gases, crystallisation, and apparently other phase transitions. They are important at the critical points of the substances, where they determine the density fluctuations and the correlation radius. All these problems are within the sphere of the concerns of modern chemical physics.

The question arises whether van der Waals molecules play any significant role in chemical reactions. At first sight, the answer should be negative, because the bond energy between the partner species is low, frequently less than kT, so that collisions with extraneous molecules induce the decomposition of the van der Waals molecules. However, the angular distribution of the reaction products in molecular beams indicates unambiguously that many reactions are preceded by the formation of an intermediate complex, whose lifetime is longer or comparable to its rotation period ($\gtrsim 1$ ps) and is much longer than the duration of the collision of the reactants. Such reactions include $Cs + RbCl \rightarrow CsCl + Rb$, $Cl + I_2 \rightarrow ICl + I$, $D + H_2 \rightarrow DH + H$, etc. The intermediate complexes in these reactions can be regarded as van der Waals molecules, because they can hardly involve any specific interactions other than the van der Waals interactions (for example in $D.H_2$, in the reaction $D + H_2 \rightarrow DH + H$). In chemical dynamics, it is assumed that such reactions proceed via a statistical complex (see Section V). Van der Waals molecules and complexes are two concepts between which it is not possible to draw a boundary in the general case. There exist, however, two approximate criteria for their differentiation—the energy and structural criteria. A complex is assumed to be a species in which the bond energy between the partners exceeds kT and can reach considerable values; if, on the other hand, the bond energy is less than or comparable to kT, such a complex is regarded as a van der Waals molecule. Furthermore, in the van der Waals molecule the interactions between the partner species are universal and non-localised; on the other hand, in the complex the interactions between the partner species are specific and localised and one can rigorously specify and demonstrate the mutual orientation of the partner species, the atoms or atomic groups through which they are bound, and the electronic orbitals which they place at the disposal of one another on "contact". For other complexes (such as complexes of metal ions with organic and inorganic ligands included within the sphere of interest of inorganic and coordination chemistry), the solution of the problem of the organisation of the partner species has long been known. For weakly bound complexes in solutions and in gases, this problem has also been solved successfully by microwave and laser spectroscopy and magnetic resonance. For example, the characteristic features of the complex formation reactions of organic radicals and molecular oxygen with organic ligands, based on the magnetic properties of the complexes and their manifestations in magnetic resonance (EPR and NMR), have been found and the structure and dynamics of these complexes have been established.

Complex formation is an old, classical problem of chemical physics and two features impart to it its modern aspect: firstly, the high level of "quantification", characteristic, as mentioned above, of the entire chemical physics; secondly, definite structural characteristics of the organisation of the partner species—how they are oriented, which orbitals participate in complex formation, and what is the topography of the complex. Behind structural problems, there is another, more important functional problem—how does complex formation modify the electronic shells of the partner species and how does it alter their reactivities? Here chemical physics endeavours to achieve a *major* aim—to employ complex formation as a chemical principle for the control of the reactivity of species, to establish the general internal relations between structure and reactivity, and to extend them to the predictive level.

Particular attention is paid in modern chemical physics to complexes of excited molecules—excimers and exciplexes. Their characteristic feature is that the bonding in them is achieved only in the excited electronic state of one of the partner species; in the ground, unexcited state, there is no bonding and this state is dissociative. The interest in these complexes is partly associated with the investigation of the pathways leading to energy relaxation, but interest is mainly concentrated on excimer lasers in which the generation threshold is reduced as a result of the emptying of the lowest level (because it is dissociative) and a high generation power is attained.

Clusters. This term combines a wide set of species containing from several atoms or molecules to several tens or hundreds of atoms or molecules, for example $(H_2O)_n$, Cu_n, Na_n, Na_n^+, Ag_n, $(OCS)_n$, Cu_n^+, $(NH_3)_n$, Bi_n, $(CO_2)_n$, $(H_2)_n$, K_n, Mg_n, Pt_n, Al_n, $(H_2O)_n(NH_3)_mH^+$, He_n, $(N_2)_n(NO^+)$, Hg_n^+, K_n, Xe_n, In_n, $Cu_nBe_m^+$ $Pt_{38}(CO)_{44}$, etc. where n and m vary from several units to 1–2 tens and for certain clusters up to several tens and even hundreds. Clusters can be atomic, molecular (comprising atoms and molecules), and mixed–atomic-molecular, neutral, or charged. They are obtained and investigated in gases (for example, in streams expanding at ultrasonic velocities), in zeolite channels (the In_8 cluster has been obtained in this way), and in solid matrices (for example, in solid argon or xenon). Fig.1 illustrates the composition of the gas clusters formed by iodine in a helium–neon mixture; the great structural variety of these species is clearly seen. They differ in composition, properties, and in the nature of the forces retaining the species within the cluster.

Clusters are comparatively new species in chemistry and their appearance is due to advances in organoelemental and organometallic chemistry in the first place and also in chemical physics (for atomic and molecular clusters). An enormous number of studies are now being devoted to the methods of synthesis of clusters and their properties and structure. Their role in the physics of condensation, evaporation, and crystallisation, where they are precursors of a new phase, a kind of "protophase", has been clearly recognised. However, the greatest interest is associated with the chemistry of these species, their reactivity, their catalytic "potentials", and their direct use in chemical materials science.

The concerns of chemical physics are concentrated on the structure and properties of these species, their spectroscopy, energetics, dynamics, stability, and conditions governing their existence. The level of "quantification" is in this instance no worse than for individual species. For example, it is known that the Cu_3 cluster is a triangular Jahn–Teller molecule with a pseudorotation barrier of 111 cm^{-1}, which is only slightly less than the energy of the zero-point vibrations (118 cm^{-1}), and a symmetrical vibration frequency of 269.5 cm^{-1}. The electronic states of this cluster, the frequencies and intensities of their electronic transitions, their geometry, etc. are known. It has been demonstrated by time-of-flight mass spectrometry that the Xe_n clusters have a preferentially eicosahedral structure with stability maxima corresponding to certain coordination numbers under the conditions of maximum close packing (the "magic" numbers $n = 13$, 19, 55, 147).

However, the main, fundamental problem (with which we began this Section on small assemblies) concerns the question how the properties of individual species evolve on combination of the latter into the properties of a substance—the properties of a new phase. This is a problem of evolution of quantity into quality and is being vigorously developed in terms of two aspects—the structural-physical and purely chemical aspects.

In the structural-physical aspect, one establishes the dependence on the structure of the cluster of its physical parameters and properties: the symmetry and type of lattice the interatomic distances, the vibration frequencies and amplitudes, the bond energies, the ionisation potentials, the Debye temperatures, the heat capacities, and the dielectric constants, and, for metallic clusters, also the Fermi levels, the spin and charge densities and their distribution within the bulk of the cluster, the electrical resistance, magnetisation, etc.

Here are a few examples illustrating the level attained in the solution of the structural "cluster" problems. Among the charged molecular hydrogen clusters $(H_2)_n^+$, obtained by the photoionisation of the neutral clusters $(H_2)_n$, only the odd ions H_{2n-1}^+ have been detected but not the even ions. On the basis of experiments and calculations, it has been concluded that the odd clusters contain at the centre the skeleton of the triangular ion H_3^+ surrounded by hydrogen molecules. The adiabatic ionisation potentials of the water molecule, its dimer, and ice vary in the sequence 12.6, 11.1, and 8.8 eV, i.e. the change in potential on dimerisation is ~40% of its total change in the transition from an isolated molecule to a substance (ice). This is also valid for the vertical potential and means that the greatest changes in properties occur in the association of the first two—three molecules. On the other hand, the ionisation potential of the Na_n clusters diminishes slowly with increase of n and its fall is accompanied by oscillations; the even members of the series have a higher ionisation potential than the odd members, but even for the Na_{14} cluster the ionisation potential is still greater (appreciably greater—by a factor of 1.5) than electron work function of metallic sodium. In the Ag_n clusters, the characteristics of the transition from molecular properties to metallic properties are manifested already for $n = 6$ (they are observed in the electronic spectra from the excitation of the surface plasmons characteristic of the metallic state), while for $n = 10–15$ the cluster becomes purely metallic.

The Fe_{15} cluster has an average magnetic moment of 2.2 μ_B per atom, while in the metal this quantity is 2.7 μ_B. Theoretical estimates yield the following distribution of the magnetic moment with respect to the bulk of the cluster: 1.1 μ_B for the central atom, 2.7 μ_B for each of the first eight neighbours, and 2.8 μ_B for each of the six neighbours of the second "rank". The electrons are also distributed non-uniformly: the central atom of the cluster has 1.27 electrons more than the surface atoms. In terms of a number of properties (the structure of the electronic spectrum, magnetism), the Fe_{15} cluster is already fairly close to metallic iron, although certain differences from the metal are observed even for the Fe_n clusters with $n > 15$).

The Cr_{15} cluster has a magnetic moment (in contrast to the metal which is anti-ferromagnetic) and the distribution with respect to its bulk is as follows: −0.7 μ_B for the central atom, +4.1 μ_B for the first neighbours, and −3.4 μ_B for the second neighbours. In metallic chromium the magnetic moment of each atom is 0.7 μ_B, i.e. the magnetic state of the central atom in Cr_{15} is the same as in the metal, while the overall magnetic moment of the cluster is determined by the magnetism of the surface atoms (the non-equality of the magnetic moments of the first and second spheres).

The structural-physical studies embrace all types of clusters—atomic, molecular, purely metallic, and organometallic, whose nucleus consists of the metal atoms and the surround is made up of organic groups. The clusters in biomolecules (for example in nitrogenase and ferrodoxin), where they are responsible for the functioning of these biomolecules, merit special attention.

We shall now discuss the chemical behaviour of the clusters (we recall that this will be done in connection with the evolution of quantity into quality). The idea of the "chemical" approach will be illustrated in relation to the proton transfer reaction. In the $(HA)B_n$ cluster, the acid molecule HA is combined with n molecules of the base B. The proton transfer from HA to B via the reaction $(HA)B \rightarrow A^-(H^+B_n)$ is detected from the appearance of the anion A^-. The question is whether this reaction depends on n and whether there is a threshold value of n at which it begins. Experiments of this type have been performed with the aid of laser spectroscopy. In the α-naphthol (HA) clusters with ammonia (B), HA is excited to the singlet state S_1. In the ground state α-naphthol is a weak acid with $pK_\alpha = 9.4$, while in the excited S_1 state it is a strong acid with $pK_a = 0.5$. The proton transfer in the $(HA^*)B_n$ cluster does not occur for $n = 1–3$ (the A^- anion is not formed). The proton is transferred only in the clusters with $n \geq 4$. In the case of β-naphthol, whose $pK_a = 2.8$ in the excited S_1 state, the same reaction occurs only in clusters with $n \geq 10$. In the $(HA).(H_2O)_n$ clusters with α-naphthol in the S_1 state, proton transfer is detected only for $n \geq 20$. Thus the question whether the cluster acquires the properties of a "phase" has a clear-cut answer, but it is not as yet general. In the examples quoted above,

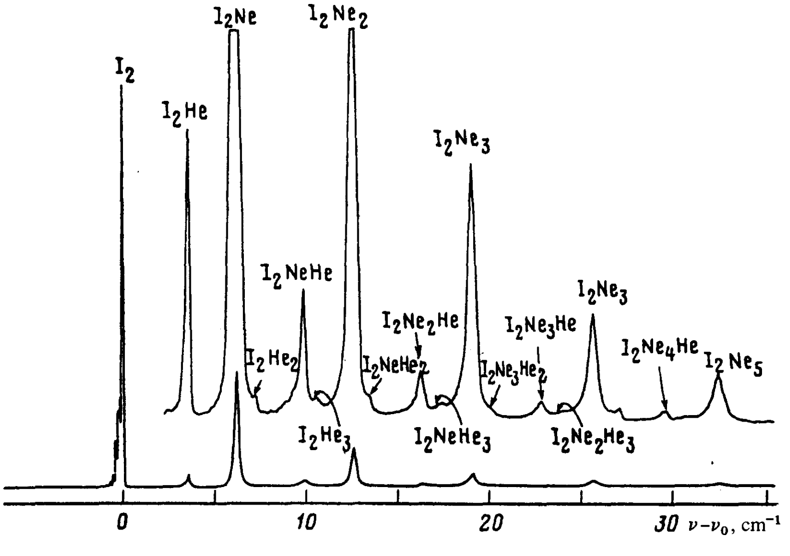

Figure 1. The fluorescence excitation spectrum of a stream of iodine vapour in a helium—neon mixture expanding at an ultrasonic velocity; the assignments of the lines to clusters having different compositions are illustrated; $\nu_0 = 17982$ cm^{-1}

the threshold value of n depends on the strength of the acid and base—the stronger the acid and base, the sooner does the cluster exhibit the features of a "phase".

For the same purpose, extensive studies have been made of the ion–molecule reactions in the clusters $(H_2O)_nH^+$, $(NH_3)_nH^+$, $(CH_3OH)_nH^+$, $(CH_3COCH_3)_nH^+$, and $(CH_3X)_n^+$ (X = F, Cl, Br, or I), and also in the mixed clusters $(CH_3X)_n^+\cdot(CO)_m$, $(CH_3X)_n^+(N_2)_m$, $(CH_3COCH_3)_n^+(CH_3OCH_3)_m$, etc. The aim of these studies was to find the characteristic features of the ion–molecule reactions (radical, nucleophilic, electrophilic) in such small assemblies, to create bridges between these reactions in gases and liquids, and to establish how the characteristics of the gas-phase reactions are transformed into those of liquid-phase processes and what is the size of the cluster when the latter begins to simulate the liquid or solid phase.

The answers to these questions are of special interest for catalysis—both homogeneous and heterogeneous. This is a problem of molecular organisation—how the atoms must be "arranged" on the surface of the catalyst and what should be their number in the cluster in order to ensure the activation of specified molecules and the catalysis of definite, selective reactions. For example, the catalytic activity of metallic gas-phase Nb_x clusters in the dehydrogenation of benzene has a threshold character: it is manifested for $x \geq 4$ and reaches a maximum for $x = 5$, 6, and 11, but it is found to be low for $x = 8$ and 10. The Nb_8 and Nb_{10} clusters also exhibit a low activity in the reactions with H_2 and N_2 and are distinguished among other clusters by their high ionisation potentials.

It is known that molecular hydrogen dissociates when it is adsorbed on metallic nickel and cobalt. However, calculations have shown that there is no dissociation in the interaction of nickel and cobalt atoms or of Ni_3 and Co_3 in the linear configuration with hydrogen. However, the Ni_3 and Co_3 triangular clusters as well as the Ni_{13} cluster do ensure dissociation. Thus the triatomic cluster with C_{3v} symmetry is the smallest, "threshold" structural element ensuring, for example, the catalysis of hydrogenation.

The problem of the evolution of quantity into quality has not so far had a general solution—neither in the structural-physical nor in the chemical aspect, but ways leading to the solution have already been found and progress on these lines constitutes one of the most important fields of chemical physics.

Special mention should be made of the chemical physics of metallic clusters in connection with the wide prospects for the application of these clusters in materials science and their use in optoelectronics and microelectronics (light filters, radiation receivers, solar batteries, composite materials, amorphous metals, new types of ferrites, etc.). [Isolated macromolecules must also be included among small assemblies. The concerns of chemical physics include the statistics of macro-molecules, internal rotation barriers, stereochemistry, optical isomerisms, the shape of macromolecules and the relative contributions of chaos and order to their organisation (coils, helices, linear chains, etc.), the interaction of macromolecules (the permeability and intertwining of coils, crystallisation, complex formation, and binding of macromolecules, including their binding to solid surfaces) "phase" transitions in isolated macromolecules (of the helix–coil type), etc. The aim of the studies of the structure and dynamics of macromolecules is to understand the principles governing the organisation of such macromolecules in block polymers, in blends, and in composite materials and to develop methods of controlling such organisation. These problems are important for ensuring the elasticity and strength of polymeric materials, for their rheology, and for the creation of new materials; here chemical physics adjoins the molecular physics of macromolecules.

3. Large Assemblies

The study of the structures of liquids and solids—amorphous and crystalline, individual components, and solutions—is the traditional task of chemical physics. The theories of liquids and solids (classical, semiclassical and quantum theories, statistical and dynamical theories), the short- and long-range order, the dynamics and the phonon spectra of crystals, the distribution function, and the computer simulation of structure and dynamics is a far from complete list of the traditional problems. The same problems are formulated in the study of disperse systems—suspensions, porous bodies, emulsions, aerosols, etc.

However, gradually the emphasis is shifting towards less traditional problems, among which most attention is being devoted to the structure of molecularly organised systems and the structure of defects and defective bodies. Thin films, adsorption layers, interfaces, liquid crystal formations, clathrates, "whiskers", monolayer and two-layer membranes, micelles, layer structures, intercalates, and Langmuir–Blodgett films—are examples of non-ideally organised structures (in contrast to crystals with their ideal organisation). The structure of these systems, their thermodynamics, the determination of the conditions governing their existence and their stability, and their behaviour in various external fields (electrical, mechanical, magnetic, and acoustic) are being investigated with the aim of deducing the principles governing the molecular organisation of such systems, the development of methods for controlling their organisation, and the prediction of the varied and useful functions of these systems.

Another modern aspect of structural chemical physics is the increasing interest in defects: impurity centres, dislocations, vacancies, molecular cavities, and local heterogeneities. New methods in chemical physics—high-resolution magnetic resonance, the annihilation of the positron and positronium, and the chemistry of muonium—are used together with traditional structural methods to analyse the defects, their nature, the structure and crystallographic environment in the vicinity of the defects, and the symmetry and amplitude of the distortions. Like isolated species, the defects are characterised by a high level of "quantification". For example, the irradiation-induced defect in zinc acetate is the radical $\dot{C}H_2CO_2(Zn)$, in which the CH_2 group executes complete rotations (jumps) around the CH_2–CO_2 bond with a barrier of 18.4 kJ mol^{-1}, while the torsional vibrations take place with an energy of 6.7 kJ mol^{-1}. This level of accuracy is typical also for the characteristics of other crystal defects.

The detection of structural heterogeneities and local cluster formation is very important for materials science; methods are being developed for non-disruptive detection. Thus the localisation of residual Si–H bonds of the cluster type has been observed in amorphous silicon (the importance of this material is generally known) by NMR. Atomic aggregates corresponding to Fe_n clusters with $n \cong 45$, in which the spin "ferromagnetic" correlation is retained at temperatures exceeding the macroscopic Curie temperature by 80 K, have been found in metallic iron from low-angle neutron scattering, i.e. the local Curie temperature is much higher than the average Curie temperature.

There is a growing interest in two extremes-completely ideal defect-free structures and highly defective structures; the latter is associated with the unusual effects and the unusual behaviour of substances under the conditions of shear deformation under pressure. In particular data are available concerning the appearance of strong paramagnetism in deformed diamagnetic metals and there has been a claim (which requires confirmation) that ferromagnetism appears in highly defective NaCl.

Structural chemical physics has self-evident aims: it "operates" on materials science—a large and most timely field of modern engineering, and is concerned with the development of principles governing the organisation of matter into specified structures and the principles used in controlling structure in order to create new generation materials with a predicted functional purpose. The strategy based on the transition from structure to properties and functions is the most reliable in modern materials science, on the basis of which considerable advances have already been achieved: new surfactants have been obtained for the large-scale removal of petroleum pollution from the surface of the sea and superconducting ceramics, organic metals, ferromagnetics, etc., have been created.

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The structure of individual chemical species and their assemblies—large and small—belongs to the set of classical problems of chemical physics. While modern chemical physics is still concerned with the solution of this problem, nevertheless most attention (priority) is given to dynamic problems, which can be grouped to a first approximation into "four types of dynamics":

1) molecular dynamics, i.e. the dynamics of the movement and displacement of species;

2) the energy dynamics, characterising the time evolution of the energy in isolated molecules and their assemblies (migration, transformation, and relaxation of energy);

3) chemical dynamics, i.e. the development of the chemical interaction of species as a function of time (including chemical kinetics as a diagnostic method for the mechanisms of chemical reactions);

4) spin dynamics, i.e. the dynamics of the population and evolution of the spin states of the reacting species.

III. MOLECULAR DYNAMICS AND MOLECULAR ORGANISATION

The important position of molecular dynamics and chemical physics is due to the following factors. Firstly, molecular movements ensure the time modulation of intermolecular potentials, i.e. they create perturbed, random ("white") or correlated noise. The Fourier spectrum of this noise determines the energy dynamics of the molecules (energy transfer and quenching of excited states, energy pumping, and relaxation). Molecular movements modulate also the magnetic interactions and they are therefore responsible for the spin dynamics and magnetic relaxation.

Secondly, molecular dynamics ensures contact between the reacting species and their appropriate mutual orientation, namely their suitable "micro-organisation" in the transition state of the reaction—not noly for diffusion controlled reactions (this is self-evident and even trivial) but also for reactions occurring under kinetic conditions (especially in solids-see Section V).

Thirdly, molecular dynamics constitutes a pathway to molecular organisation; it is not fortuitous that both concepts are considered here together in a single Section. One cannot say that molecular organisation is a function of molecular dynamics alone, that only dynamics organises structures. Molecular organisation is determined primarily by thermodynamics and its laws. However, among molecularly organised systems (including biomolecules), non-equilibrium systems occupy a major place (they are in fact as a rule of greatest interest) and their formation, stability, and, what is still more important, their functioning are determined by molecular dynamics. Finally, the most important factor is that the dynamics of translational, rotational, and orientational movements of the structural elements of substances and materials (electrical and magnetic dipoles, electrons, ions, and molecular fragments) determines the properties of materials—mechanical strengths, elasticity and plasticity, rheology, electrical conductivity, magnetism, dielectric strength, etc.

1. Molecular Dynamics

The theoretical methods used in the analysis of molecular dynamics are just as varied as the experimental methods. The task of the theory is to find ways for the correct description of diffusion, to establish a relation between the "microscopic" dynamics and the transport macroproperties of the medium, and ultimately to impart a predictive power to the theory. A number of approaches have been developed for the solution of this problem. The self-diffusion coefficient D is expressed in terms of the autocorrelation velocity function $z(t) = \langle u_x(t).u_x(0)\rangle$, where u_x is the x component of the velocity of the selected species; in its turn, the function $z(t)$ is related to the radial distribution function and the frequencies of the harmonic oscillations of the given species in the medium. Its detailed behaviour is investigated by the computational methods of molecular dynamics based on the synthesis of the trajectories in the movement of the species by the numerical integration of the classical equations of motion. The validity of the approximations in the selection of the parameters and the function $z(t)$ is estimated by comparing the theoretical and experimental values of D. For low densities of the medium, $z(t)$ decreases as $t^{-3/2}$, while for high densities its behaviour is complex, oscillatory, and analytical predictions are difficult.

The dynamics of a Brownian particle (i.e. a large and heavy particle placed in a medium comprising small and light particles) constitutes a traditional problem. Such a particle does not respond to individual impacts by the molecules in the medium and its dynamics is controlled by the random fluctuations of the forces acting on its surface. The equation of motion has the classical form of Newton's second law:

$$mu = F\,[t, u(t')] \quad ,$$

where the velocity u and the force F at time t depends also on the velocity $u(t')$ in the preceding instant t'. Depending on whether there is a correlation between the past and the present (i.e. a correlation between t' and t) and its form, the solutions assume different forms. The search for these solutions at different correlation levels and comparison of their predictions with the experimental reality constitute in essence the subject with which the theory is concerned.

If the characteristic time of the fluctuations F is short compared with the velocity decay time, then F depends solely on $u(t)$ and there is no correlation between the past and the present. This situation is described by the familiar simple Langevin equation in which the force and the coefficient of friction are calculated. This problem is again solved at different approximation levels for the autocorrelation velocity function and the force, for the distribution of the initial velocity u_0, etc. In one of the approximations (u is small and the liquid is incompressible), one finds, in particular, the familiar Stokes–Einstein relation. For high velocities, the characteristic velocity decay time is $\sim 10^{-13}$ s, i.e. is of the same order of magnitude as the time taken by a sound wave to traverse the intermolecular distance. The Stokes approximation then fails and account must be taken of the elastic properties of the medium and the high-frequency spectrum of the elastic vibrations: this is the familiar Zwanzig–Bixon approximation.

The simple Langevin equation predicts an exponential decrease of the autocorrelation velocity function, which is not correct. This means that one cannot neglect the correlation between t and t'. The equation taking into account the correlation between the past and the present is known as the generalised Langevin equation, which includes the correlation time function—the memory function. It takes into account the fact that the species considered creates in the course of its movement a perturbation at time t', which extends in time and at the instant t returns to its source. The choice of the memory function, its various approximations, and the solutions of the generalised Langevin equation employing these functions constitutes one of the developing theoretical fields.

Another field is concerned with the development of the kinetic theory in which the probability density in the phase space of the coordinates and velocities and its time evolution are calculated. This density takes into account the correlation between the velocity and momentum. In the case of frequent but weak "soft" collisions, the movement of the species is described by the familiar Fokker–Planck equation, whose solutions are obtained and analysed at different approximation levels and subject to different initial conditions. In the case of infrequent and strong collisions with a large transfer of momentum, the movement is described by the Boltzmann equation (if it is assumed that there is no correlation with respect to the coordinates and velocities between the Brownian particles and the particles constituting the medium) or by the Enskog equation is a spatial correlation is retained.

The simple Langevin equation and the Fokker–Planck equation describe the behaviour of large particles for which the fluctuating driving force arises from the frequent and weak impacts by the species in the medium. The Boltzmann–Enskog equations describe the second limiting situation of the rare and strong binary collisions without any correlation between them. In a real situation, the theory cannot ignore the dynamic correlation between the collisions and in this sense the generalised Langevin equation with its memory function corresponds most adequately to reality. However, the difficulty is that the memory effects and the correlation between the past and the present are taken into account semiempirically with selected memory functions. The *ab initio* derivation of these functions from first principles is a difficult and unsolved part of the many-body problem. The task if theoretical molecular dynamics therefore remains the creation of bridges between the dynamics of an individual collision and the long-period dynamic behaviour of the species.

At the level of the theoretical approaches examined, solutions are being obtained to the problem of the Brownian movement with different dimensions—one-dimensional, two-dimensional, and three-dimensional—for the description of the behaviour of species in narrow channels and porous media, on surfaces within thin films and membranes, and in liquids and solids. Many studies have been devoted to the dynamics of pairs and to the calculation of the probability of their reaction or annihilation; this problem is particularly timely for radical pairs—neutral and charged, with and without allowance for spin evolution, with and without allowance for the acceptance and decomposition of radicals, with unrestricted diffusion and with diffusion limited by a closed volume with absorbing or reflecting walls. The solutions are used in photochemistry and in the chemical physics of magnetic-spin effects.

The generalised Langevin equation is solved in different versions, with different memory functions, and there exist classical and quantum solutions. The dynamic problems are solved for different intermolecular potentials and the effects of the anisotropy of the potential, the contribution of attraction and repulsion, and the role of short-range and long-range parts of the potential, its Coulombic and exchange branches, are analysed. Many problems are associated with the collective dynamics of crystal lattices, networks, liquid crystals, and membranes and with the dynamic behaviour of quasi-particles—phonons, solitons, magnons, plasmons, and excitons. Theoretical problems of molecular dynamics are frequently at the junction with the problems of contiguous fields of physics—the theory of elasticity and relaxation, plastic deformation, thermal conductivity, and rheology.

The scope of the experimental research into molecular dynamics is almost limitless; it refers to the transport of molecules in liquids, the transport of atoms in metals and alloys, the drift of electrons and ions in semiconductors and liquid and solid electrolytes, and diffusion in porous, microheterogeneous, and molecularly organised systems (micelles, clusters, adsorption layers, membranes, and Langmuir–Blodgett films). Studies on the dynamics of phase formation, especially in the early stages of this process under precritica conditions and at the critical points, and the dynamics of aggregation, coagulation, and cluster formation occupy an important place.

An independent field of study is associated with the dynamics of macromolecules—synthetic and biological: the conformational dynamics of neutral molecules and polyelectrolytes, the kinetics of helix–coil transitions, the "breathing" of macromolecular coils, the dynamics of the entanglement and disentanglement of coils, the untwisting of helices and of binding to substrates, the local dynamics of segments and the "macrodiffusion" of large molecules, etc. All these questions refer directly to polymer materials science, to the problems of the physics and mechanics of polymeric materials, and, for biomolecules, to the problems of their functioning (the synthesis of proteins, DNA, RNA, enzyme catalysis, muscle contraction, the permeability of membranes, bioenergetics, and immunological recognition).

Surface diffusion constitutes an important branch of dynamics associated with the problems of the growth and perfection of crystals, epitaxial layers, and films and with the problems of adsorption and heterogeneous catalysis. Appriciable advances in this field have been ensured by ion-field microscopy of surfaces whereby one can observe single atoms and follow events involving them. Thus the diffusion coefficient of Ba on tungsten changes by several orders of magnitude on different planes and the activation energies for diffusion on the (110), (111), and (112) planes differ sharply: 5.0, 11.5, and 17.5 kcal mol^{-1} respectively. On the face-centred lattice of rhodium, the atoms of the latter on the (111) plane migrate already at 55 K, while on the (110) plane they begin to move only at 300 K. The activation energies for diffusion also differ greatly: $\varepsilon(111) = 3.6$, $\varepsilon(311) = 12.4$, $\varepsilon(110) = 13.9$, and $\varepsilon(100) = 20.2$ kcal mol^{-1}. Under these conditions, the entire difference between the rates is determined by the energetics, the contribution of the entropy component being constant. On corrugated surfaces [of the (110), (311), and (331) types], the diffusion is directed strictly along definite channels—the potential energy ravines. The properties of the self-diffusion of platinum and tungsten are the same.

On the surface of body-centred lattices, new features appear in diffusion; in particular, along certain planes [for example, Rh (111)], the diffusional behaviour of a pair of atoms differs from the behaviour of a single atom, i.e. a correlated movement appears and gives rise to new problems concerning the ratio of the individual and collective movements and their contribution to diffusion. The W, Re, and Ir atoms on the W(211) surface move in pairs; the Pt_2, Pt_3, and Pt_4 clusters (which are linear) move on the W(110) plane via jumps of single atoms with retention of correlations in pairs and clusters.

Surface two-dimensional dynamics is an actively developing field in chemical physics. It refers not only to solid surfaces but also to monomolecular films on liquids (lateral diffusion), to membranes, and other two-dimensional systems. Here the main interest concerns the problem how the characteristics of two-dimensional dynamics are related to the atomic structure of the planes, to the molecular organisation of the two-dimensional systems, and to their thermodynamics and structure.

Excellent physical methods are used to investigate molecular dynamics: Rayleigh and Raman light scattering, acoustic and magnetic relaxation, the annihilation of positrons and positronium, coherent and non-coherent scattering of cold neutrons, laser picosecond and femtosecond spectroscopic methods, and also mathematical methods for the modelling of molecular dynamics. Laser picosecond holography merits special attention. The idea of this method involves the optical generation of a short-lived holographic lattice in a liquid or solid and subsequent observation of the dynamics of the "dissipation" of this lattice. The holographic lattice is created by passing through the liquid or crystal two picosecond pulses, coinciding in time, which cross in the specimen at an angle θ. Their interference creates in the specimen a holographic lattice with a constant $d = \lambda/2\sin(\theta/2)$, where λ is the wavelength of the laser emission generating the lattice. The principle governing the appearance of the holographic lattice involves the formation of electronically excited states, the excitation of intramolecular vibrations, and the generation of acoustic waves (phonons). Regardless of its specific cause, the holographic lattice constitutes a spatial-periodic change in the refractive index. Such a lattice "dissipates" after a time owing to molecular diffusion, the energy relaxation, or the decay of waves, while the dynamics of the dissipation can be detected by means of a delayed laser probe beam, which is diffracted by the holographic lattice. The intensity of the diffraction as a function of the delay of the probe beam yields the kinetics of the dissipation of the lattice on a picosecond scale. The characteristic dissipation times can be obtained from the time variation and the spatial scale of the dynamic processes responsible for the dissipation of the holographic lattice and the spatial averaging of the refractive index can be obtained from the frequency dependence (because d depends on λ).

The transport of excited molecules, their energy relaxation, the energy transfer (the transfer times and distances), the generation and detection of coherent acoustic phonons in crystals, and the rate at which they spread along different crystallographic axes are investigated in this way and the same procedure is used to observe the vibrational overtones and to measure the elastic and photoelastic constants of crystals. The method can be used for the non-disruptive monitoring of optical materials (including fibres) and for the analysis of the dynamics of membranes, liquid crystals, and amorphous bodies.

2. Molecular Organisation

Continued interest in molecularly organised systems has become a new feature of modern chemical physics. Molecular and supermolecular organisation of *ensembles* of species is an important principle governing the regulation of chemical processes and constituting a major resource in chemical technology and materials science. So far, this principle has been developed and adopted to only a slight extent, but its potential is exceptionally great and there are grounds for the claim that in the future "organised" chemistry will occupy a leading place in technology and materials science.

Studies on these lines are so wide in scope that it is impossible to analyse them fully. Even a cursory listing of selected examples gives an idea about the scale of such research at all levels—from molecular to macroscopic and supermolecular. The organisation of molecules into complexes, their incorporation in clathrates and micelles, immobilisation, the creation of organised systems simulating biochemical systems (biomimetic systems), the molecular organisation of active centres in metalloenzymes (nitrogenase, ferredoxin), clusters, intercalates, and layer structures—this is only a limited series of examples of organisation at the molecular level. The conformational organisation of macromolecules (helix, coil, extended chain, and their combinations) determine their packing in polymeric materials and specify the physicomechanical properties of fibres, block and regular copolymers, and blended compositions: the problem is how is this achieved, what is the form of the bridges between organisation and properties, and how their interrelation should be controlled.

Conformational dynamics, complex formation, and molecular organisation of polyelectrolytes, which have opened up major prospects for the creation of a new generation of immunogens and vaccines, in which it is possible to bypass even the genetic control of the immune response occupy a special place, i.e. it is possible to ensure that only B-lymphocytes are active, bypassing the T-lymphocytes responsible for the genetic prohibition of immunogenesis.

Phase organisation and phase transitions are traditional physicochemical problems which are still far from being solved. For example, it is known that there is a short-range order in the structure of simple liquids, in the organisation of which atomic configurations with odd (fifth) order symmetry elements predominate, while in a crystal lattice no matter how small, there should be symmetry elements with even orders only; there is virtually no understanding of the liquid–crystal transition with a rearrangement of the symmetry.

The answers to the following questions are of fundamental importance for the creation of materials with a regulated structure, with a specified combination of elastic and plastic properties, etc.: how to predict the fusion curve, the pVT diagram, and the thermodynamics of the phase transition from the intermolecular potentials; what is the microscopic mechanism of crystallisation, which factors control crystallisation, supercooling, and glass formation, what are the mechanisms of first- and second-order phase transitions and their relation with the short- and long-range order potentials; what are the contributions of the individual and collective molecular dynamics to phase transitions, and how is phase microheterogeneity created and how does it develop.

For example, the structure and organisation (both molecular and spin, magnetic organisation) of solid oxygen have attracted much attention. The existence of several phases in solid O_2 has been established experimentally and the reasons for their stability and magnetic properties have been determined: the orientationally disordered paramagnetic γ-phase; the antiferromagnetic β-phase with long-range orientational order and molecular axes parallel to the C_3 screw axis; the antiferromagnetic, monoclinic α-phase with two mirror magnetic sublattices. Theoretical analysis of the lattices with allowance for the magnetic component of the potential and the Heisenberg exchange spin–spin attraction predicted new stable phases with unusual magnetic properties. The importance of these studies does not lie merely in the prediction of new magnetic phases in solid O_2; it is much more important that the principles of molecular and spin organisation, which ensure specified magnetic properties, have been deduced in relation to this example. These principles are also important for the creation of organoferromagnetic materials, organic semiconductors, metals, and superconductors, ferromagnetic alloys, glasses, and various ceramics (including superconducting ceramics).

The phases and phase transitions in two-diemensional systems, especially in adsorbed layers, are even more varied. The ways in which the species on the surface are organised, the reorganisation of the two-dimensional structure to form a three-dimensional structure and conversely, the order–disorder transitions (fusion–crystallisation), the decomposition into domains and clusters, the dynamics of the surface migration of the domains, and the correspondence or lack of it between the organisation of the adsorption layers and the structure of the lattice of the solid (commensurate and non-commensurate phases) are important in this instance.

Many physical methods, including the diffraction of slow electrons and optical generation of the second harmonic are used to investigate the organisation and dynamics of a two-dimensional lattice gas and phase states and transitions. For example, it has been established on the basis of electron diffraction that hydrogen adsorbed on the Ni(111) plane forms an ordered two-dimensional phase for coverages of 0.3–0.5 and at a temperature below 250 K; for other coverages and for $T > 250$ K the adsorbed layer is disordered and non-organised.

The interest in two-dimensional organisation is targeted towards adsorption and adsorbents and heterogeneous catalysis and catalysts; but there is also another aim—the creation of surface layers with unusual properties by incorporating atoms in the upper layers of the lattice. For example, when a gold layer on silicon is bombarded with Ar^+ ions (100 keV), a mixed Au/Si layer is created and the intermettallic compound Au_3Si is formed. This is a non-equilibrium metastable phase which does not exist under equilibrium conditions. When titanium and zirconium phosphates are bombarded with Ar^+ ions, the surface layers are depleted in oxygen and phosphorus atoms, which are driven to the lower "levels" of the lattice.

The questions which fall within the range of concerns of chemical physics are how atoms are dislodged as a result of impact by an ion, how the electron shells are shaken in this process and how energy and momentum are lost, what are the secondary reactions of the hot atoms and electrons of the target, and how the atomic layers of the lattice are reorganised. The organisation and reorganisation of the surface layers of solids by ionic implantation of plasma and laser "microsurgical" methods constitute a promising pathway to the modification of the surface and the imparting of unusual mechanical, anticorrosion, magnetic, electrochemical, electrophysical, and photosensitive properties, which constitutes the principal stimulus of the research into this branch of chemical physics.

Numerous chemical and physicochemical processes occur at interfaces and the atomic-molecular organisation of the latter is associated with their functioning. The optical generation of the second harmonic is known to occur in non-centrosymmetric crystals, but the second-order optical non-linearity arises also at the boundary between two centrosymmetric media if a symmetry gap occurs in the interface. Since the thickness of the interface is much smaller than the optical wavelength, the dipoles induced at the interface form a polarised layer generating the second harmonic. This method is sensitive to the structure of the interfaces and ordered monolayers, to their dynamics with a small time resolution, to surface reconstruction, and to phase transitions. For example, Langmuir–Blodgett layers, their "evaporation" (liquid–gas-like two-dimensional state transition), and their "fusion" (two-dimensional "liquid"– two-dimensional "solid" transition) have been investigated by this method. The anisotropy of the polarisation tensor has been measured for a monolayer of pentadecanoic acid on water and it has been shown that, for low coverages, the molecules are inclined to the water surface at an angle of 30° while with increase of coverage they "straighten out" and in the limit lie along the normal to the surface.

The monolayers of docosanoic acid on aluminium and carbon form a two-dimensional hexagonal lattice, in which the molecules are perpendicular to the surface of the support and, when the number of monolayers increases to 7, the molecules are inclined and the hexagonal lattice is transformed into an orthorhombic lattice, whereupon one can observe the evolution of the phase transition. The phase transitions in biological membranes and their relation with the cooperative rotational movements of the hydrocarbon chains, the electrical double layers on electrode surfaces, etc. can be investigated in this same way. The first attempts have been made to create monolayers which are two-dimensional ferromagnetics.

Molecular and supermolecular organisation is a characteristic property of biochemical processes (the synthesis of proteins and nucleic acids, photosynthesis, ion transport, enzyme catalysis, immunological responses, electron transport, phosphorylation, etc.). Enzymes bind and orient reagents, organising the elementary chemical steps and ensuring a high stereoselectivity, as well as selectivity with respect to the reagent, the type of reaction, its localisation, temperature, pH, etc. Not only the elementary steps but whole sequences of reactions are organised in biochemical processes. The selectivity and productivity of biochemical processes reach a level which is only rarely attained in the usual chemistry (for example, polymerisation on immobilised catalysts) precisely by virtue of the high degree of organisation.

This situation is recognised with increasing clarity and there has been a sharp growth of interest in organised systems and their "chemical" functioning in recent years. The characteristics of chemical reactions in liquid crystals, layers, membranes, micelles, clathrates, clusters, etc. are being widely investigated. Organised catalytic systems are being constructed in accordance with the principles of enzyme catalysis and biomimetic processes simulating the operation of biosystems are being developed.

The self-organising systems in which the molecular organisation is induced by the chemical reaction are especially attractive. For example, the colourless molecule of a spiropyran dye with a long hydrocarbon "tail" is transformed photochemically into the merocyanine dipolar coloured form with separated charges, the molecules combining into micelles only in this form. The pohtochemical reaction functions in this instance as a trigger which "switches on" micelle formation.

The reaction can also "switch on" phase transitions (for example, the crystallisation of a solvent on nuclei—the molecules of the reaction product). This principle of the chemical trigger makes it possible, in particular, to increase by many orders of magnitude the sensitivity of the photodetecting systems (for example, in photography). An example of a "natural" chemical trigger is provided by the photoisomerisation of rhodopsin, which induces conformational transformations in the protein opsin, and the latter initiates a cascade of enzymic reactions, which ultimately lead to the generation of a membrane potential and the visual reception of light in the retina of the eye.

The most striking examples of supermolecular organisation have been observed in chemical reactions and crystals. For molecules organised into a crystal, their intrinsic reactivity, which is controlled by the structure of the electron shell, proved to be much less significant for the reaction than the mode of packing—the arrangement of the molecules in the crystal. The mode of reaction is determined by the intermolecular distances in the crystal, the mutual orientation of the molecules, and the spatial symmetry of the crystal. There are a number of examples of the unique selectivity and topological directionality of the reactions in crystals, which are atypical for the usual reactions in liquids or melts. Many organic substances have several (sometimes up to 10–12) crystal-chemical modifications. In fact, one can speak of the creation of a new branch of chemistry—the crystal-engineering chemistry, whose task is to construct crystals programmed for a specified type of chemistry.

Just as striking examples exist in heterogeneous reactions. Thus the Fe(111) plane is 430 times more effective in the synthesis of ammonia from H_2 and N_2 than the (110) plane and is 13 times more active than the (111) plane. On the Pt(111) plane, hexane is converted into benzene, while on the (100) plane cyclic and branched saturated hydrocarbons are formed from hexane. The molecular organisation of crystals or lattice atoms on the surface does indeed "write the script" of the chemical reaction in this instance.

IV. ENERGY DYNAMICS

In terms of the scale of research, energy dynamics occupies a leading place in chemical physics and such research has two major aims. The first aim is to create the theoretical foundations for and to develop the principles of selective, "non-statistical" chemistry ensuring a directed activity and specified reactions of the molecules (plasma-chemical activation, laser "surgery" of the molecules, energy stimulation of reactivity). The second aim is to search for ways of storing energy in the internal degree of freedom of molecules (electronic, vibrational, and rotational) in order to create new lasers, including lasers with solar pumping.

Energy dynamics includes a wide range of problems: selective population of rotational, vibrational, and electronic states, the exchange and transfer of energy between various states within the molecule and intermolecular exchange, and the relaxation of internal energy to kinetic and lattice energy. Here these problems will be considered briefly in terms of the following logical arrangement: the energy dynamics in gases and on the gas–solid surface, where it is possible to differentiate the individual contacts between species and to identify more reliably the physical interactions responsible for the fate of the energy; this is followed by the energy dynamics in van der Waals molecules and clusters as intermediate structures in which many-species interactions are switched on; finally, we have the energy dynamics in large assemblies—in liquids and solids.

1. Energy Dynamics in Gases

This is the most thoroughly developed and most vigorously developing field; the main cause of interest in it is the comparatively small number of contacts between energy-rich species (particularly at low pressures), their long lifetime, and hence good conditions for the storage, control, and utilisation of energy.

The exchange of the electronic energy (*E*) of excited atoms for the vibrational (*V*), rotational (*R*), and translational (*T*) energy of the molecules is a fundamental process in the energy dynamics of plasma, interstellar lasers, and many chemical gas-phase processes. The energy exchange via different channels (*E–V*, *E–R*, *E–T*) and different mechanisms, the time scale of the exchange, and the cross-sections of the channels depend on a multiplicity of causes, the most important of which is the mechanism of the exchange and the topology of the potential energy surface of the initial and final states of the system of interacting partners.

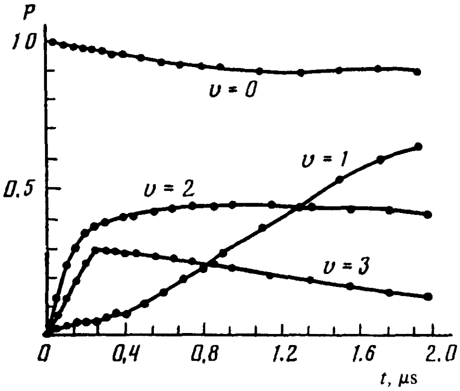


Figure 2. Dynamics of the population *P* of the vibrational states of the hydrogen molecule for $J = 1$ after the laser pumping of Na atoms (in relative units); 570 K, $p_{H_2} = 1$ bar, duration of laser pulse 0.2 μs.

The *E–V* exchange can proceed via a direct "physical" mechanism without the rupture of chemical bonds or via "chemical" mechanisms. Thus the Na($^2P_{1/2}$) atom, with a cross-section almost identical with the gas-kinetic cross-section, transfers its electronic energy to the vibrational-rotational levels of the H_2, N_2, CO, NO, O_2, I_2, C_2H_4, etc. molecules. These processes are investigated by laser spectroscopy: the pulse from one laser pumps the Na atoms (for example, in a mixture of sodium vapour and hydrogen) and the probing pulses of the second laser, with a variable time arrest, probe the populations of the vibrational-rotational states of the H_2 molecules and their time evolution. The Na($^2P_{1/2}$) atom pumps the vibrational state of H_2 with $\nu = 1, 2, 3$ (populations of 13, 61, and 26% respectively) in accordance with complex kinetics, which depend on ν, an example of which is illustrated in Fig.2. It constitutes a complex interplay of processes involving electronic-vibrational exchange between Na and H_2 and the migration of the *V*-energy via the vibrational reservoir of the H_2 molecules. The rotational distribution for different ν depends also on the rotational quantum number *J* (Fig.3), the states with odd *J* being populated to a greater extent than those with even *J*. In the *E–V* exchange between Na($^2P_{1/2}$), on the one hand, and N_2, CO, and NO, on the other, the high vibrational states up to $\nu = 3–5$ (in the interaction with N_2 and CO) and up to 7 (in the interaction with NO) are populated. The CO states with $\nu_{max} = 5$ are populated in the Hg($^3P_1$) + CO process.

It was assumed that the E–V exchange in the A + BC system proceeds via the ionic state $A^+ ... (BC)^-$ and that the ionic energy level intersects the energy levels of the initial and final states, the points of intersection ensuring the resonance energy transfer. However, *ab initio* calculations of the potential energy surfaces (PES) for Na + H_2, Na + N_2, and Na + CO have shown that this mechanism does not operate. The non-adiabatic transitions (the E–V exchange) occur in the region of the intersection of the ground ($^2A_1$) and excited ($^2B_1$) PES in the C_{2v} configuration for Na^*H_2 and Na^*N_2 (Na is attached at right angles in the middle of the H_2 and N_2 bond) and in the $C_{\infty v}$ configuration for Na*CO (linear configuration). In this region the molecules are in the extended phase and after decomposition of the complex remain vibrationally excited.

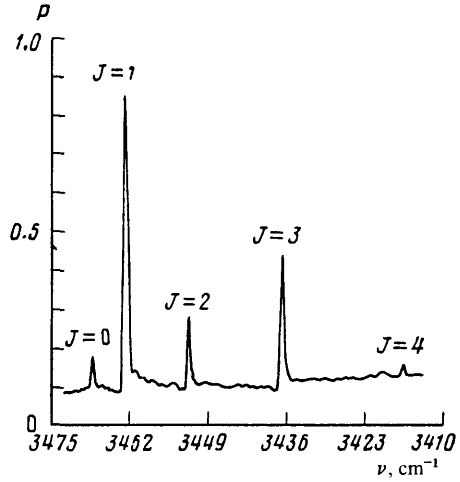


Figure 3. The spectrum of the rotational states of the hydrogen molecule for the $\nu = 3$ level after the laser pumping of Na atoms; delay time 0.5 µs, 500 K, $p_{H_2} = 300$ mbar (P = relative population).

For Na + H_2, the contribution of the "chemical" mechanism of the quenching of an electonically excited atom (via the formation of the hydride NaH) is not more than 0.5%. For the Mg(^{1,3}P), Ca(^{3}P), Sr(^{3}P), and Zn(^{1,3}P) atoms with energies in the range 2–5 eV, the chemical mechanisms involving the formation of the hydrides MH predominate, the reactions occurring via the insertion of the atom in the molecule in the C_{2v} configuration and with rotational excitation of the hydride MH (for example, the states with $J \geqq 30$ are populated in MgH).

The second chemical mechanism is dissociative:

$$Hg(^3P_1) + H_2 \rightarrow Hg(^1S_0) + H + H \ .$$

The energy transfer (the E–E process) makes an important contribution to the quenching, for example:

$$Hg(^3P_1) + Tl(^2P_{1/2}) \rightarrow Hg(^1S_0) + Tl(^2S_{1/2})$$

or

$$Hg(^3P_1) + C_2H_4 \rightarrow Hg(^1S_0) + C_2H_4(^3\Pi_1)$$

with transfer of angular momentum. The E–E processes are important for the pumping of lasers. For example, the functioning of the oxygen–iodine laser is based on the reactions

$$I_2(^1\Sigma_g^+) + O_2(^1\Delta_g, v \geqslant 3) \rightarrow 2I(^2P_{3/2}) + O_2(^3\Sigma_g^-) \ ,$$
$$I(^2P_{3/2}) + O_2(^1\Delta_g) \rightarrow I(^2P_{1/2}) + O_2(^3\Sigma_g^-) \ ,$$
$$I(^2P_{1/2}) \rightarrow I(^2P_{3/2}) + h\nu \ .$$

The conditions for energy resonance are critical for the transfer of the E-energy.

Rydberg atoms (see Section II) are attractive because the conditions for the resonance of small quanta of the E-energy with the V- and R-energies of the molecules are fulfilled in their collisions with molecules and the laws governing the E–E and E–R processes are conveniently investigated in relation to these atoms.

A Rydberg atom can be approximated by a model in which the Rydberg (excited) electron is so remote from the ionic residue of the atom that it can be regarded as a virtually free particle and the collision of the atom with the molecular target can be treated as the interaction of three particles—the Rydberg electron, the ionic residue, and the target particle. It can be accompanied either by the direct E–V or E–R transfer or by the reverse T–E,V–E, or R–E transfer, which increases the quantum number n of the Rydberg atom up to its ionisation threshold. The laser-induced fluorescence and selective-field ionisation methods have been developed for the investigation of these processes.

The interaction of the Xe(27f) atom, in which $n = 27$ for the f electron, with HF proceeds in accordance with the scheme:

$$Xe(27f) + HF(J) \rightarrow Xe(n, l) + HF(J-1)$$

i.e. the HF molecule loses a rotational quantum and the Rydberg atom is excited to the states with $n = 40$ and 41 and different values of l and $|m_l|$. This excitation is very selective: the Xe(n, l) states with $n = 39$ or 42 are absent, since the energy deficiency for them is approximately 5 cm^{-1}, while for $n = 40$ and 41 it is much less: ~1.2 and ~2.1 cm^{-1}.

The interaction of the Xe(27f) atom, in which $n = 27$ for the f electron, takes place for $J \leqq 3$. For $J \geqq 4$, i.e. for a larger store of the R-energy, the atom ionises:

$$Xe(27f) + HF(J) \rightarrow Xe^+ + HF(J-1) + e \ .$$

However, Xe(23f) behaves in a completely different way:

$$Xe(23f) + HF(J=0) \rightarrow Xe(21, l) + HF(J=1) \ .$$

Unlike the previous instance, here the electronic energy is transferred to the rotational levels of the target and the Rydberg atom undergoes partial deactivation with decrease of n. In this case the deficiency of energy resonance amounts to ~1.5 cm^{-1} and this process does not take place with the Xe(26f) and Xe(27f) atoms; although their energies are greater than that of Xe(23f), the resonance deficiency of ~2.6 cm^{-1} completely suppresses this process.

Together with the E–R processes, virtually isoenergetic processes involving no change in n and J also take place, for example:

$$Xe(27f) + HF(J) \rightarrow Xe(27, l) + HF(J)$$

in which the change in the orbital electronic momentum is compensated by the change in the translational energy.

The E–V transfer is a still more markedly resonance process. Thus the Na(ns) Rydberg atom induces a rigorously resonance-type vibrational excitation of CH_4 and CD_4: the transition $5s \rightarrow 4p$ (energy 2930 cm^{-1}) excites only the ν_3 vibration in CH_4 (2940 cm^{-1}), the $6s \rightarrow 4p$ transition (1331 cm^{-1}) induces the ν_4 vibration in CH_4 (1340 cm^{-1}), and the $7s \rightarrow 5d$ transition (975 cm^{-1}) excites the ν_4 vibration (965 cm^{-1}) in CD_4. The orbital angular momentum then changes by $\Delta l = 1$ or 2; processes with $\Delta l = 0$ do not occur. Thus the energy of the transition 8s → 7s coincides with that associated with the frequency ν_4 in CD_4, but this energy resonance is insufficient to effect the $E-V$ process.

These examples contain a small proportion of what is now known about the atomic-molecular energy dynamics and demonstrates merely the multiplicity of factors involved in this problem, the level of its solution, and the pathways leading to it. The same situation exists also in the energy dynamics of molecules: the examples quoted below give merely an idea about the current state of the problem and about the ways in which it is solved and the aims which have inspired the search for such solutions.

The relaxation of small molecules at low vibrational levels has been thoroughly investigated and has been incorporated in textbooks and monographs. Further progress in this field is being directed to complex molecules and high energies: the characteristic features of relaxation, the mechanisms, and the dynamics are being established. For example, Fig.4 shows how the vibrational energy of acetylene "descends" down the levels and is converted into kinetic energy: there is initially a rapid redistribution among the initial vibrational states (less than 15 collisions are necessary to achieve this), after which follows the slow relaxation of the symmetrical ν_2 stretching vibration (~650 collisions are required) to the ν_4 and ν_5 deformation vibrations, which slowly discard the V-energy into the R- and T-forms. A remarkable feature of this approximate picture is the "bottleneck" effect in the ν_2 vibrations, which can store energy for a long time.

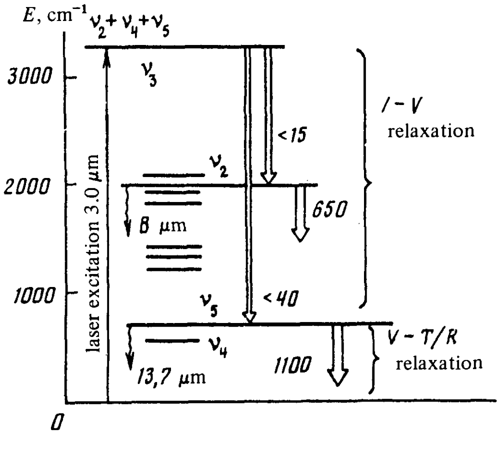


Figure 4. Pathways leading to the relaxation of the vibrational energy in the acetylene molecule among vibrational levels; the numerals against the arrows indicate the number of collisions of the excited molecule required for relaxation from the given level.

Molecules capable of retaining energy are needed for gas lasers and especially for lasers with solar pumping. Natural laser effects are known in the atmospheres of certain planets and the creation of solar lasers constitutes an attractive prospect. The principal requirements which must be met by gases to be used as media in solar lasers are as follows: wide and as far as possible continuous absorption bands to ensure effective pumping; the presence of metastable states and the occurrence of relaxation processes ensuring an inverted population; stability (or capacity for regeneration) of the chemical composition of the laser medium.

In order to find systems capable of transforming solar energy and storing it at excited levels with an adequate density, exceeding the generation threshold, it is essential to know not only the physicochemical structure of the molecules (see Section II), but also their energy dynamics—the lifetimes of the excited states, the mechanisms and cross-sections of the physical and chemical relaxation, and the ways of transforming energy. Examples of solar lasers based on Br_2, I_2, Na_2, Cs_2, IBr, etc. already exist, but their characteristics are far from perfect.

Rotational energy is known to be discarded rapidly, giving T-energy even in collisions with inert gas atoms, since the distances between the rotational levels are small compared with kT. However, for molecules with a small moment of inertia or with a large store of rotational energy (large J), the distances between the rotational levels are comparable to or exceed kT. Under these conditions, the molecule rotates so rapidly that its potential appears to be isotropic to the approaching atom. On the basis of this principle, the atom exhibits a weak perturbation and is ineffective in the $R-T$ relaxation. Because of this factor, the highly excited states of hydrogen halides survive many collisions and lasers based on rotational transitions have been devised using them.

Frequently such molecules with an inverse population of the R levels are formed in photochemical pumping. Thus the photolysis of BrCN at 193 nm yields CN with low E- and V-energies but with a large store of the R-energy (up to 1400 cm^{-1}); the states with J from 30 to 86 are populated under these conditions and the yield of molecules at the maximum of the distribution with respect to J ($J_{max} \cong 60$) is ~4%. These states are metastable (their relaxation by Kr, Ar, N_2, CO, and Xe is relatively inefficient) and are suitable for lasers.

For the majority of polyatomic molecules, the key problem is the intramolecular distribution of energy with respect to the vibrational reservoir. The intramolecular vibrational relaxation (IVR) is a collision-free process resulting from the intramolecular interaction of oscillators—vibrations of different types and having different frequencies. IVR determines the processes leading to the decomposition of molecules and ions on excitation by electron impact or photoexcitation, in chemical activation, and on multiphonon excitation; IVR influences strongly the vibrational and electronic-vibrational fluorescence spectra, chemiluminescence spectra, and the spectroscopy of laser systems.

Excellent methods (picosecond and femtosecond laser spectroscopy) for the generation of coherently pure vibrationally excited states in both electronic ground and electronically excited states have been developed.

A remarkable feature of IVR is the retention of coherence on redistribution and migration of energy among levels, which is manifested by quantum beats, observed on the kinetic luminescence decay curves. The frequencies of the quantum beats are related to the number of levels involved in the energy exchange and the coefficients of the basic vibrational wave functions, from which the overall vibrational wave function of the molecule is made up, can be found from the phase shifts and the amplitude of the modulation of the beats. Furthermore, the Hamiltonian matrix describing the interaction between the oscillators can be found, in principle, on the basis of these beat frequencies and coefficients.

For example, in the anthracene molecule for low vibrational energies (up to 1200 cm^{-1}) there is almost no energy redistribution, the quantum beats are missing, and the vibrational states generated by the laser excitation relax monoexponentially with $\tau \cong 20$ ns. When the vibrational energy store is 1380–1520 cm^{-1}, strong quantum beats appear with a frequency of ~5 GHz, indicating energy migration in which several levels with migration times of several hundreds of picoseconds are involved. For larger energies, rapid monoexponential loss of the coherence of the initial vibrational states takes place owing to the rapid migration of energy with $\tau \cong 20$ ps.

The redistribution of the V-energy is extremely selective: by no means all the vibrational states participate in the energy exchange. Thus, for a V-energy of 1380 cm^{-1}, only three vibrations interact strongly and participate in the energy exchange, while the density of the vibrational levels corresponding to this energy is ~25 per cm^{-1}, which is characteristic also of other energies in the vibrational reservoir. The number of levels participating in the exchange is much smaller than the density of the vibrational states. Such selectivity of the exchange is associated with the fact that the vibrational states are coupled via the anharmonicity of the vibrations and the latter can obey definite symmetry conditions. Thus, for anthracene (D_{2h} symmetry), this implies that the given vibrational state is coupled by anharmonicity to only $^1/_8$ of the total number of vibrational states.

The population of the rotational levels of the given vibrational state accelerates the vibrational migration and the IVR but does not alter the overall features—the coherence and quantum beats are retained. In principle, one may select on this basis the interaction responsible for the IVR—the anharmonicity of the Coriolis forces. Clearly, if the latter make the main contribution to the energy migration, then the beat frequencies must depend greatly on the rotational temperature and conversely, the absence of such dependence may imply a leading contribution by the anharmonicity.

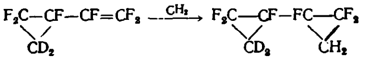
The establishment of the IVR laws is one of the current growing points in energy dynamics. This problem has a direct bearing on the molecular mechanics of vibrations, namely on the question of the relation between coherence and chaos in the vibrational motion of molecules with different stores of vibrational energy. It adjoins the problem of the ergodic nature of molecular systems, which arises in the classical mechanics of Hamiltonian systems of coupled anharmonic oscillators. The famous KAM (Kolmogorv, Arnold, Moser) theorem demonstrates that, for small perturbations (and small energies), the classical movement of anharmonic oscillators is quasi-periodic and regular, whilst for high energies it becomes chaotic. Thus, for the Hamiltonian

$$H=\frac{1}{2}(p_x^2+p_y^2+\omega_x^2x^2+\omega_y^2y^2)+\lambda x(y^2+kx^2),$$

the trajectories (x, y) corresponding to small energies are periodic (Fig. 5b), while for high energies they become chaotic (Fig. 5a); here x and y are the coordinates, p_x and p_y the moments, and ω_x and ω_y the frequencies.

The relative contributions of order and chaos in IVR depend on the store of the vibrational energy, on the anharmonicity constants of the oscillators and their coupling, and on the density of the vibrational levels. The questions how IVR arises—coherently or chaotically—and at what rate are of fundamental importance for chemical dynamics. Both the pathways leading to the dissociative decomposition of the molecule and the energy pumping of the fragments depend on whether the IVR occurs before the decomposition or whether the decomposition overtakes IVR. In the former case the reaction is described by the statistical theory, while in the latter the reaction takes place "non-statistically", selectively.

As a rule IVR predominates in the competition between IVR and the dissociative decomposition. Thus, in the selective laser excitation of CH_2FCH_2Br, the yield of HBr and HF on decomposition of this molecule corresponds to a statistical distribution of the vibrational energy. In the selective pumping of the fifth overtone of the vibrations of the OH group in the $(CH_3)_3COOH$ molecule, the preferential breakdown of the O–O bond takes place; the energy transfer to this bond occurs over a period of ~2 ps, i.e. before the reaction via the O–H bond. In chemical activation via the exothermic addition of the carbene, i.e.



$$F_2C\!-\!CF\!-\!CF\!=\!CF_2 \ (CD_2) \xrightarrow{CH_2} F_2C\!-\!CF\!-\!FC\!-\!CF_2 \ (CD_2)(CH_2)$$

the vibrational energy, localised initially in the right-hand three-membered ring, is found in the left-hand ring after ~1 ps and the reactions of this molecule occur after IVR.

The number of examples of the non-statistical decomposition or vibrationally excited molecules is much smaller, but they open up pathways to photoselective chemistry, to the laser surgery of molecules, and to "non-statistical" chemistry. Naturally, there exist only limited possibilities for controlling the rate of IVR, but even the knowledge of the

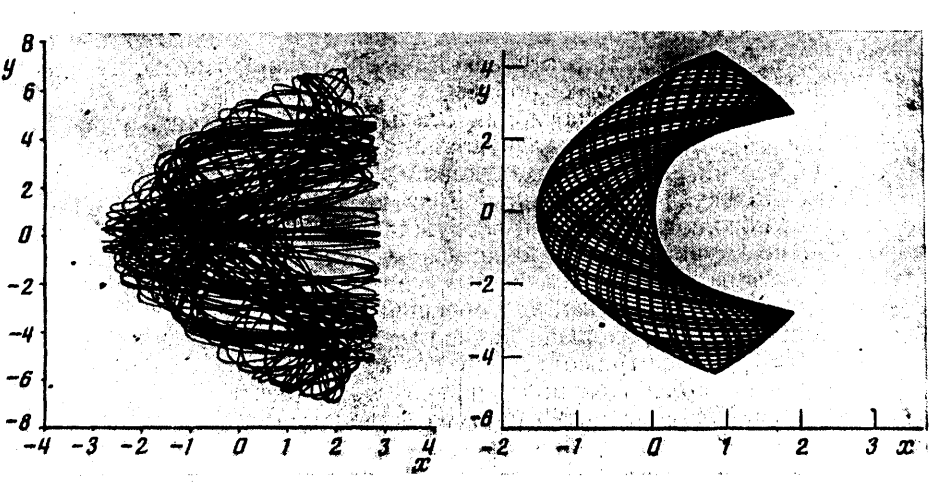


Figure 5. The chaotic (a) and quasi-periodic (b) trajectories $y(t)$ and $x(t)$ of the Hamiltonian H; $\omega_x = 2\omega_y$.

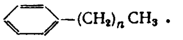
characteristic features of IVR is sufficient to be able to predict which molecules and in which processes are suitable for photoselective chemistry. The identification of the possibilities and principles of the molecular energy organisation of photoselective chemistry is one of the intriguing problems of chemical physics.

The advances in laser spectrocsopy have led to the possibility of investigating the vibrational relaxation of electronically excited states. The method of the ultrasonic expanding flow, in which the flux of molecules with rotational and vibrational temperatures close to the absolute zero is excited by the laser to specific vibrational levels of the electronically excited state and the fluorescence arising from these levels and its decay as a function of time are then detected, has been developed most thoroughly.

The width of the vibronic fluorescence bands increases sharply with increase in the store of the vibrational energy, starting from a certain threshold. This is evidence for a rapid intramolecular vibrational distribution—a rapid escape of vibrational energy from the populated level to a multiplicity of others as a consequence of the anharmonicity of the vibrations and Fermi resonance. When the number of coincident levels (and Fermi resonances) is small, coherent excitation results in the appearance of vibrational quantum beats corresponding to the oscillation of energy between the levels which modulates the decrease of the fluorescence intensity. Incidentally, such beats are also observed in intermolecular energy transfer. Thus, on excitation of HCl in argon, at an overall pressure of 3 bar and an HCl partial pressure of 29 mbar, the $H^{35}Cl$ vibration is pumped at 2963.3 cm^{-1}. Owing to the coherent energy transfer between $H^{35}Cl$ and $H^{37}Cl$ during the time decay of the signal of the trial pulse probing the population of the excited vibrational states, a periodicity (quantum beats) is observed with a period of 15 ps, which corresponds exactly to the difference between the vibration frequencies of the isotopic forms of HCl, amounting to 2.22 cm^{-1}. Under these conditions, the phase coherence is retained much longer, about 50 ps.

If the density of the Fermi resonances is large, there is a pronounced superposition of beats with a large set of frequencies and this situation is referred to as "Fermi bleeding" in IVR. Thus in naphthalene in the S_1 state in the presence of an excess vibrational energy $E_V = 3068$ cm^{-1}, the density of the vibrational levels is about 1600 per cm^{-1}, the distance between the levels involved in the "Fermi bleeding" is about 0.06 cm^{-1}, and the characteristic IVR time is 10–100 ps. In fluorobenzene the energy threshold of the intense IVR is much lower and begins at a density of levels amounting to 40 per cm^{-1}. In this case the Coriolis interaction, involving the rotational levels in IVR, which increases the density of the levels by the factor $2J$ (for rotational quantum number J), makes a significant contribution.

The role of the density of levels in IVR is illustrated by the popular example of molecules of the type



On excitation of the symmetrical vibration at 993 cm^{-1} of the electronically excited benzene ring, the time taken for the store of the V-energy to leak from the ring to the "tail" of the molecule depends on the density of the vibrational states of the "tail", i.e. on the value of n. Thus, for $n = 1$, this time is long, about 900 ns, whereas for $n \geqq 4$, it is reduced to 2–10 ps.

The electronic relaxation of even polyatomic molecules is a much slower process and it is investigated by laser spectroscopic methods with the same high level of "quantification" as the structure of the excited states (see Section II). Thus in benzophenone the electronic energy is lost from the S_1 state (the S_1–S_0 transition) over a period of 50 ps, the transition from the T state to the S_0 state via thermal excitation to S_1 (slow fluorescence) takes place in 1 μs, and the spin-prohibited direct T–S_0 relaxation requires a time of ~1 ms. The rate of relaxation of the E-energy then depends on the store of the vibrational energy in a complex manner. For example, in 9-cyanoanthracene in the presence of an excess of E_V up to 800 cm^{-1}, the quantum yield of the luminescence from S_1 and the luminescence time τ depend little on E_V: $\tau \cong 26$ to 28 ns. When $E_V \cong 1200$–1750 cm^{-1}, both the quantum yield and τ decrease sharply with increase of E_V and, when $E_V \cong 2000$–2500 cm^{-1}, the quantum yield diminishes to 0.1 and τ to 4 ns.

The energy dynamics of the molecules in the gas phase is a multifactorial, multiparameter problem in which none of the factors is of secondary importance: the type of molecules (diatomic, or polyatomic, linear or non-linear), the type of process (intramolecular or intermolecular), the type of energy (E-, V-, R-, or T-reservoir), and the sequence of the energy migration and escape processes (within one reservoir or between reservoirs), the mutual influence of the reservoirs, the anisotropy of the potential of the molecules and the processes ensuring its modulation, the limitations and prohibitions based on the angular momentum, the symmetry and deficiency of the energy, and the rate of movement of the partner species in the region of the overlap of their potentials. The theoretical solution of the problem requires the knowledge of the potential energy surfaces of the ground and excited states and calculations on the dynamics of the motion of the molecular system along the surface—both these problems refer to chemical dynamics (see Section V).

Analogous problems arise in the energy dynamics of the molecules on the surface—namely the problems of the rules governing the transfer of the vibrational, rotational, and electronic energy on impact of the excited molecule against the surface, of which phonons participate in the energy exchange processes (the collective lattice phonon or the localised high-frequency vibrations of the surface atoms), of the ways in which these processes depend on the velocities and masses of the molecules and on the potentials of the molecule and the target, and of the role played by the "roughness" of the surface on the atomic scale.

The greatest experimental progress has been achieved in this instance by the employment of the method of molecular beams, where a monochromatic stream of atoms or molecules in specified quantum states is directed onto the surface and the velocity and angular distribution of the reflected or desorbed species as well as their new distribution among quantum states are then determined. These studies have now assumed a large scale and they are aimed at the fundamental problems of heterogeneous catalysis, the chemistry and physics of surfaces, plasma chemistry, as well as the branches of thermophysics engaged in the questions of the thermal protection of space devices.

2. Migration of Energy in Clusters

The acquisition, storage, and utilisation of energy by molecular systems of finite dimensions (van der Waals molecules, clusters) have become the subject of vigorous investigations quite recently; the interest in this problem is associated with the fact that in such systems the energy spectrum can vary continuously as the dimensions are altered and this leads to the possibility of creating bridges between the energy dynamics of isolated species and the energy dynamics of species in large assemblies (liquids and solids).

The pumping of energy into clusters is achieved by electron impact, by electron capture, or by the laser excitation of one of the species in the cluster. For example, in the van der Waals complex $I_2.He$, the iodine molecule is promoted by the laser to an electronically excited state with an excess of vibrational energy and probe pulses then detect the fate of the energy and the dynamics of its migration. The principal migration pathway is the transition to the low-frequency vibration of the complex and dissociation, for example:

$$I_2 \cdot He(v=7) \rightarrow I_2(v=6) + He\ .$$

i.e. one vibrational quantum is sufficient for dissociation. The time taken for energy transfer from the high-frequency to the low-frequency vibration is fairly long but it decreases sharply with increase of the energy store. Thus, for $I_2.He$ with v = 12, 18, 23, and 25, the time taken for the escape of a vibrational quantum varies in the sequence 200, 100, 50, and 40 ps. Hence it follows that the anharmonicity of the vibrations, which is greater for larger amounts of vibrational energy, is responsible for the energy transfer.

However, this is not the only factor controlling the energy dynamics of clusters. The size of the vibrational quantum, the symmetry and structure of the cluster, the resonance deficiency, and the density of the vibrational states are also important. For example, the time of the vibrational relaxation to dissociative levels is ~100 ps in the $I_2.He$ cluster and ~100 ns in the H_2Ar cluster, i.e. is greater by three orders of magnitude; this is caused by the weaker interaction of the two types of vibrations in $H_2.Ar$ compared with $I_2.He$. For the same reason, the rate of dissociation in the $(HF)_n$ (n = 2 - 6) clusters (the rate at which HF is split off) in the presence of the enormous excess of vibrational energy of 3000 cm^{-1} amounts to only 10^6–10^7 s^{-1}. In the cluster of pentacene with Ar an energy of 300 cm^{-1} in the aromatic ring is converted slowly (over a period of 10–30 ns depending on the number of Ar atoms in the cluster) into the low-frequency vibration modes of the Ar atoms.

The intermolecular energy transfer and relaxation in gases are frequently preceded by the formation of van der Waals molecules or clusters whereupon new and unexpected features appear. Thus, in order to discard an energy quantum of the HCO deformation vibration, not less than 1500 collisions with the N_2 molecule are necessary but only 10 collisions with NO are sufficient. One might suspect that in the latter case a chemical reaction serves as a powerful relaxation channel, but this is not the case, since the reaction is slow and, furthermore, it is retarded on deformation-vibrational excitation of HCO. It is most likely that relaxation takes place in the complex HCO.NO in which the deformation vibration frequencies of HCO and the low-frequency vibrations of the complex itself do not differ greatly and the energy rapidly slows down to the dissociative levels of the complex.

The relaxation of the energy in clusters has begun to be investigated also by the theoretical methods of molecular dynamics. As an illustration of this approach, we shall consider the Ar_{13} clusters in which the electronic energy is "injected" into one of the central atoms. It organises a localised state—the Ar_2^* excimer, where one of the atoms is of the Rydberg type. The dissociation energy of the excimer, the equilibrium state, and the parameters of the Morse potential are known; next, its interatomic interaction with other atoms of the cluster is "switched on" and the molecular and energy evolutions of the cluster are analysed.

The redistribution of the vibrational energy in the cluster is hindered by two factors: (1) the marked difference between the vibrational frequencies of the excimer and the atoms in the cluster; (2) the local expansion of the cluster around the excimer, occurring when the intermolecular potential is switched on, because the repulsive branch of the excimer–argon atom potential is much steeper than the repulsive potential between the argon atoms. As a result of this, the first stage of the energy relaxation is the "explosion" of the cluster—its rapid expansion (over a period of ~200 fs) around the excimer. The second stage is the slow migration of energy to the vibrational mode of the cluster with its localisation at the predissociation levels of the surface atoms; as a result, the atoms "evaporate" from the cluster and the vibration energy is converted into the kinetic energy of the leaving atoms. This process takes place over a period of 10–100 ns.

The characteristic features of the relaxation of the highly excited (Rydberg) atoms in the lattice, the main one being the local "explosion" of the lattice, can be seen from this example; this is important for the problem of the interaction of strong radiations (laser, electronic, and X-ray) with solids (explosive evaporation, surface erosion, etc.).

The energy dynamics of the clusters aroused increasing interest and has been stimulated by the well-founded hope that the fundamental problems of energy relaxation in liquids and solids can be solved on the basis of the cluster energetics.

3. Energy Dynamics in Liquids

The fluxes of vibrational energy in a liquid are controlled by more complex laws than in a gas or a solid. In gases the vibrational pumping and relaxation are regulated by binary collisions—elastic (when the vibrational states of the partner species are not altered and there is only a shift of the phase of the vibrations) or inelastic (where both the vibrational states and phases change). The first process corresponds to phase relaxation, i.e. to the loss of phase coherence (characteristic time T_2); the second process involves energy relaxation—the removal of the energy to the lattice (characteristic time T_1). The T_1 process determines the escape of energy from the vibrational reservoir to the lattice, while the T_2 process constitutes the migration of energy within the vibrational reservoir without its loss to the lattice.

In a solid, both the phase and the energy relaxation can be interpreted as the interaction of a local vibration (or a vibrational exciton) with the phonon spectrum of the lattice (of a crystal or glass), whereupon the approximation of harmonic phonons is frequently satisfactory.

A liquid is too dense for the treatment to be restricted to the approximation of binary collisions but it is not sufficiently ideal to allow the phonon model to be employed. Furthermore, in a liquid there are low-frequency degrees of freedom (of rotation and of oscillation of the centre of gravity) for which $\hbar\omega \leq kT$ and which can be treated in classical terms as well as high-frequency degrees of freedom ($\hbar\omega \gg kT$), which must be treated only in quantum terms.

The phase coherence of the excited states assumes special importance for the energy dynamics in a liquid, where the density of oscillators is high. The rapid loss of phase coherence implies the rapid migration of the energy in the reservoir, whence $T_2 \ll T_1$. The ratio of T_1 to T_2 is important also for another reason—the energy can be extracted in the form of laser emission only under the conditions of high coherence. If the phase relaxation is limited by the escape of energy to the lattice, then $T_1 = T_2$; in this case, each step involving the removal of a quantum to the lattice also implies the loss of coherence.

For a set (packet) of oscillators of one kind (with one frequency and one phase), the absorption or emission line corresponding to the given vibrational transition is homogeneous (or homogeneously broadened) with a width T_2^{-1}. For a set of packets, the line constitutes a superposition of the lines of the individual packets; this is an inhomogeneous (or inhomogeneously broadened) line. The causes of the loss of phase coherence are various. Firstly, there is the microstructural inhomogeneity of the liquid when the oscillators in different local environments and the phases fall out of step at different rates under different conditions. This is especially significant for rapid phase relaxation, where molecular dynamics is incapable of averaging out the microstructural inhomogeneity during a period shorter than T_2. Secondly, there is the resonant transfer of vibrational quanta between oscillators; each step involving the migration of a quantum is accompanied by a loss of phase coherence. Thirdly, the intramolecular interaction of oscillators with anharmonic coupling between them can also become a cause of the system going out of phase: the excitation and relaxation of one oscillator modulate the frequency and phase of another oscillator. Other causes are the vibrational-rotational interaction, Fermi resonance, and the formation of clusters.

In the energy dynamics in a liquid, one can trace the same trend as in clusters: the greater the frequency isolation of the oscillator, the longer the period during which it retains the energy. A striking example is provided by the N_2 molecule in liquid nitrogen for which T_1 at 77 K has the record value of 45–60 s, while $T_2 \cong 150$ ps, i.e. $T_1/T_2 \gg 1$. In the presence of admixtures (CO, CO_2, CH_4, O_2), the relaxation of N_2 is directed to impurities and from them to the lattice. For SO_2 in liquid SO_2, we have $T_1 \cong 45$ ns and it is independent of temperature, while for HCl ($\nu = 1$), $T_1 \cong 1-2$ ns in liquefied HCl and decreases with increase of temperature. The HCl ($\nu = 1$) relaxation cross-section in liquid xenon is 3×10^{-8} and is almost the same as in a gas for collisions with argon atoms. In CH_3F, the ν_3 vibration has a relaxation time of 375 ns in liquid O_2 and 1300 ns in liquid argon.

In polyatomic and "low-frequency" molecules, the relaxation times are shorter by several orders of magnitude and lie in the picosecond range. Thus the CH stretching vibrations in CH_2Cl_2 and CH_3COCH_3 lose energy over periods of 50 and 65 ps and these are nevertheless long times, because the deformation vibrations are of the low-frequency type and the Fermi resonance is suppressed. In CH_3OH, the second overtone of the CH_3 deformation vibration has virtually the same frequency as the stretching vibration and the Fermi resonance shortens the relaxation time of the stretching vibration to 1.5 ps. In ethanol, the Fermi resonance is slightly weakened and T_1 increases to approximately 20 ps. In $CHCl_3$, $T_1 \cong 115-140$ ps and depends on temperature; for SF_6, $T_1 = 27$ ps in liquid oxygen and 160 ps in liquid argon.

The vibrational relaxation of polyatomic molecules as a rule takes place in two stages: (1) rapid redistribution of energy among the vibrational modes (or their combinations) within the molecule over a period of 1–2 ps and (2) slow escape of energy from the vibrational reservoir to the lattice over a period of tens or even several tens of picoseconds. For example, in anthracene and azulene, the intramolecular migration of energy via vibrations takes place over a period of 1–2 ps and the removal of energy to solvent molecules takes 20–40 ps.

Rapid intramolecular energy fluxes are associated with a high density of the vibrational states and a strong interaction (via anharmonicity and Fermi resonance). Thus, for molecules containing ~30 atoms, the density of the vibrational levels is ~10^6 per cm^{-1}. The slow relaxation is associated with the transfer of the *V*-energy to the librational and translational degrees of freedom of the solvent molecules and this reservoir is "disconnected" from the vibrational reservoir as regards frequencies.

The study of the energy relaxation in large molecules in both ground and excited states has steadily advanced to the femtosecond region; the aim of such advance is to find new possibilities for laser-coherent effects and for selective "non-statistical" chemistry.

The theory of vibrational relaxation in a liquid has developed predominantly in two directions. The first originated from the gas model of binary collisions into which "collective" elements are introduced—correlations of pairs, triplets, etc. The second direction employs the model of collective movements and the rate of relaxation is determined in terms of the Fourier components of the correlation functions of the non-diagonal matrix elements of the perturbing Hamiltonian. A purely hydrodynamic theory based on model representation of a species "trembling" in a viscoelastic medium has also been developing; the theory reproduces collectively the effects of viscosity and density, but it is too simplified to reproduce all the characteristic features of the relaxation. An approach based on the generalised Langevin equation (see Section III) has also been developed. In all cases the theory is based on intermolecular interactions and the relaxation is a result of a complex interplay of attractive and repulsive forces; the prediction of the result of this interplay and the determination of its rules and characteristics is a complex and serious combined problem in molecular and energy dynamics.

4. Energy Relaxation in Solids

The relaxation and transfer of electronic energy in solids (especially in crystals) is a thoroughly developed field of physics and chemical physics with long traditions. The principal laws governing the transfer and quenching of energy and the mechanisms of its degradation have been formulated, the dependences of the transfer cross-sections on the oscillator strengths, on the distances between the donor and the acceptor, and on the orientation of the dipole moments of the optical transitions of the donor and acceptor are being refined, and the characteristic features of the electronic relaxation in excimers and exciplexes are being investigated. The aspects of this problem associated with photosynthesis, phosphors, and solid lasers are developing particularly vigorously.

In vibrational relaxation, the main problem is the dynamics of phonon excitations and the relaxation of the vibrationally excited impurity centres as reflected in the phonon spectrum. The lifetimes of the optical phonons in crystals are measured by coherent laser spectroscopic methods; thus in diamond their lifetimes T_1 are 2.9 and 3.4 ps at 295 and 77 K respectively and the A_{1g} vibration of the CO_3^- anion in $CaCO_3$ relaxes over a period of ~3 ps.

The relaxation of impurity centres is of interest for the same reasons that the centres themselves are of interest (see Section II). The "burning of holes" in an inhomogeneously broadened spectrum (optical or vibrational), i.e. the saturation of optical or vibrational transitions for the given packet of centres of molecules, is used for their investigation. Conclusions about the rates and mechanisms of relaxation and about the contributions of the T_1 and T_2 processes to the relaxation are reached on the basis of the elemination of the "hole".

Direct results can be obtained from the spectroscopy of impurity centres in single crystals. For example, the width of the lines in the vibrational spectrum of SiF_6 in a xenon single crystal at 14 K is 0.028 cm^{-1}; it is homogeneously broadened, i.e. all the SiF_6 molecules in the xenon crystal are identical and constitute a single vibrational packet. The line width is determined by T_2, i.e. by the loss of phase coherence as a result of the phase falling out of step in the elastic scattering of the lattice phonons by the vibrations of the impurity centres (SiF_6 molecules).

Furthermore, it is possible to discover which phonos are responsible for the phase relaxation. At low temperatures (14–50 K), the temperature dependence of the line width (T_2^{-1}) is described satisfactorily on the assumption that the local phonons with the following parameters are responsible for the phase coherence: frequency 4 cm^{-1}, lifetime 8 ps, constant for the coupling of the SiF_6 vibrations to local phonons 0.08. At high temperatures (>50 K), the bulk-phase (Debye) phonons of the crystal play the main role with a coupling constant of 0.05 and a frequency maximum of 42 cm^{-1} (this corresponds to a Debye temperature of 62 K). For ReO_4^- in ionic crystals of alkalis, the line width is also determined by T_2^{-1} and the phase coherence is lost to Debye phonons.

One of the new aspects of the energy dynamics in solids is the relaxation of charge carriers and excitons in semiconductors. For example, the pulse excitation of carriers (duration of pulse 50 fs) in the GaAs superlattice (65 periods in GaAs having a thickness of 96 Å with barrier layers of $Al_{0.3}.Ga_{0.7}As$ having a thickness of 98 Å) generates a packet of excited carriers, whose relaxation takes place over a period shorter than 100 fs. The average energy of the carrier then remains unaltered, i.e. only energy exchange between the packet of excited carriers and the remaining carriers in the conductivity band takes place during 100 fs. The elimination of energy and the descent of the carriers to the bottom of the conductivity band take place over a period of the order of picoseconds (over a period of ~5 ps in GaAs) and the relaxation to the valence band requires ~7 ps.

The examples presented here are few in number but they demonstrate the high technical level of the experiments and the high time and frequency resolution. Little has been done as yet in energy dynamics in solids, but progress in this field is constantly accelerating.

V. REACTION DYNAMICS

This is the science of the development of chemical processes in time, which constitutes the central component of chemical physics. It answers or attempts to answer fundamentally important questions such as which reactions can occur and which are prohibited, in what ways and by what means is it possible to remove the prohibition, how chemical reactions can be controlled, and how the rate and direction of the reaction can be influenced. Chemical dynamics is the fundamental basis for the creation of new and the improvement of existing technologies. A second important aspect of chemical dynamics is analysis of the ways of transforming energy in elementary reactions in order to search for high quality chemical laser systems.

1. Potential Energy Surfaces and Theories of Reaction Dynamics

The task of the theory is the development of methods for the calculation of rate constant or cross-sections for specified quantum states of the reacting species; potential energy surfaces (PES), i.e. the dependence of the total energy of the reacting atomic-molecular system on the coordinates of the atoms, are needed for this purpose. The PES is the "conductor" of the chemical reaction, controlling the trajectories of the transitions from reactants to products and determining the reaction channels, the reaction cross-sections, and the distribution of energy in the product.

The calculation of PES is the first problem of chemical dynamics. Non-empirical (*ab initio*) computational methods are being developed; they are laborious, since they require the calculation of a large number points on the surface, but the main difficulties are associated with the correct allowance for the electronic correlation energy. Furthermore, subsequent employment of this PES in the calculation of trajectories requires an analytical, functional representation of the entire PES (which is virtually impossible) or of its section in the vicinity of the trajectory to be calculated. Semiempirical quantum-chemical methods are also being developed (for example, the method of diatomic complexes in the molecule—DCM), but the most popular are the even simpler methods based on the familiar London equation for the energy of a triatomic system. Among them, the LEPS (London–Eyring–Polanyi–Sato) PES is widely used. Semiempirical methods for the calculation of the one-dimensional profile of the reaction path from the reactants valley to the products valley are also known (for example, the "bond energy–bond order" method); it is useful in approximate calculations where only the rate constants are of interest and the entire PES need not be known.

Examples of PES for the $O + H_2$ reactions are presented in Fig.6. For linear $O(^3P) + H_2$ collisions, the forms of the PES obtained by the *ab initio* and DCM methods differ. The crossing point in the former is displaced towards the valley of the initial reactants and in the latter towards the valley of the products. This difference is of fundamental importance for the possibility of activating this reaction and the fate of the energy. It is seen from Fig.6*c* and 6*d* that the PES for the reaction $O(^1D) + H_2 \rightarrow OH + H$ with a linear configuration of the atoms and for the insertion reaction $O(^1D) + H_2 \rightarrow H_2O$ differ sharply from the PES for the $O(^3P) + H_2$ reactions.

The accuracy of the PES is a painfully acute problem in chemical dynamics: any errors in the calculation and distortions in the PES entail marked deformations of the trajectories. The reaction trajectories and cross-sections are so sensitive to the details of the PES that one frequently resorts to the solution of the converse problem: the trajectories and cross-sections are assumed on the basis of a calculated PES and then the results of the calculations are compared with reliable experimental data and the PES is "corrected" until "satisfactory" trajectories reproducing the experimental data are obtained.

The construction of the PES is the first part of chemical dynamics; the second part involves the calculation of the trajectories in the movement of the reaction system on the surface. If the calculation is based on the equations of classical mechanics, then the procedure is called the method of classical trajectories; if the quantum states of the internal degrees of freedom (rotations and vibrations) are taken into account in the equations, then the trajectories obtained are assumed to be quasi-classical in the sense that their initial conditions take into account the quantum character of the rotations and vibrations, but they do not represent rigorous solutions of the quantum equations of motion.

Examples of quasi-classical trajectories for the reactions $C(^1D) + HI \rightarrow CH + I$ and $C(^1D) + HI \rightarrow CI + H$ are presented in Figs.7*a* and 7*b*. Both trajectories describe the mutual approach of three atoms (the C atoms move along the normal to the centre of the H–I bond) with formation of a complex having a lifetime of ~0.8 ps along the first trajectory and ~0.4 ps along the second. The periodic changes in interatomic distances, i.e. bond vibrations (between 0.5 and 1.3 ps) are very marked in the complex; the highest frequency is that of the C–H vibration and the lowest frequency is that of the C–I vibration. The lifetime of the complex is comparable to the time required for the intramolecular migration of the vibrational energy (see Section IV) and its statistical distribution therefore holds in the reaction products.

The trajectories of the same reactions occurring in a linear collision do not reveal the existence of a complex. They have the form typical for the generalised reactions A + BC → AB + C (Fig. 7c). The absence of a long-lived bound state in such reactions is the cause of the non-statistical distribution of energy in the products.

The method of quasi-classical trajectories does not take into account the quantum effects of the motion and of the tunnelling under the barrier. Such problems do not arise in quantum calculations, being exotic rather than usual. The experience gained in the calculations has demonstrated that the introduction of quantum corrections to the quasi-classical trajectories with a one-dimensional potential barrier is insufficient and that it is necessary to solve the problem with a multidimensional barrier and that a method capable of describing the classical movement of the reactants along the PES over long distances and tunnelling over short distances is needed.

Definite advances have been made on these lines: a method of complex trajectories has been developed, within the framework of which it is possible to combine the mutually exclusive concepts of tunnel and classical trajectories. A complex trajectory becomes real when the real time is replaced by the imaginary time ($t \to it$) and the PES is replaced by the inverted PES ($U = -U$). In this method there are difficulties associated with the choice of the boundaries and contour of the trajectories, but overall it is an effective procedure whereby one can obtain "quantum" results from quasi-classical equations of motion.

Calculation of the trajectories on a single PES is frequently insufficient, since there are several PES in very close proximity in individual regions or even quasi-intersecting. The unusual problem of allowing for the non-adiabatic nature of the process, i.e. for the "jump" of the reaction system

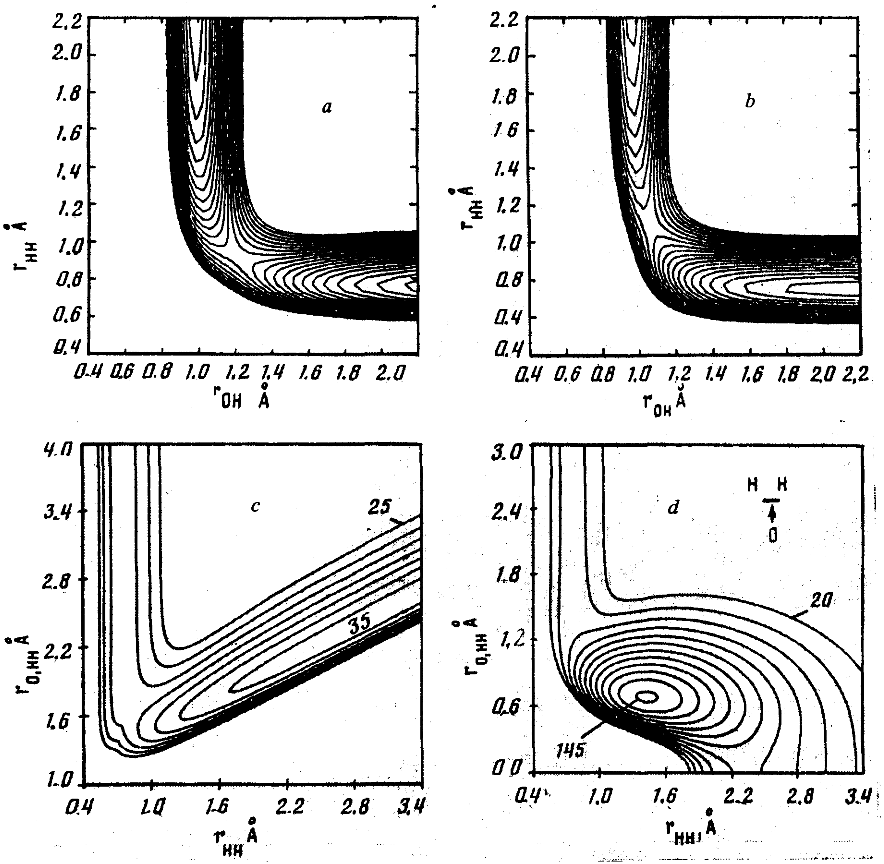


Figure 6. The potential energy surfaces for the O + H_2 reactions: *a*) non-empirical PES for $O(^3P)$ + $H_2 \to OH + H$ (linear complex, r^*_{OH} = 1.216 Å, $r^*_{H_2}$ = 0.920 Å, 12.58 kcal mol^{-1} barrier); *b*) PES obtained by the DCM method for $O(^3P) + H_2 \to OH + H$ (linear complex, r^*_{OH} = 1.061 Å, $r^*_{H_2}$ = 1.103 Å, 13.35 kcal mol^{-1} barrier); *c*) PES obtained by the DCM method for $O(^1D) + H_2 \to OH + H$ (linear complex, $r_{O,HH}$ = distance from O to the centre of the H–H bond, $r^*_{O,HH}$ = 1.66 Å, r^*_{HH} = 0.78 Å, 0.80 kcal mol^{-1} barrier); *d*) PES obtained by the DCM method for $O(^1D) + H_2 \to H_2O$ (complex with C_{2v} symmetry, reaction involving the insertion of O in the centre of the H–H bond, no barrier). Constant energy lines have been drawn from 1 to 20 kcal mol^{-1} at 1 kcal mol^{-1} intervals (for *a* and *b*), from 35 to 25 kcal mol^{-1} at 10 kcal mol^{-1} intervals (for *c*), and from −145 to 20 kcal mol^{-1} at 15 kcal mol^{-1} intervals (for *d*); r^* = coordinates of the apex of the barrier.

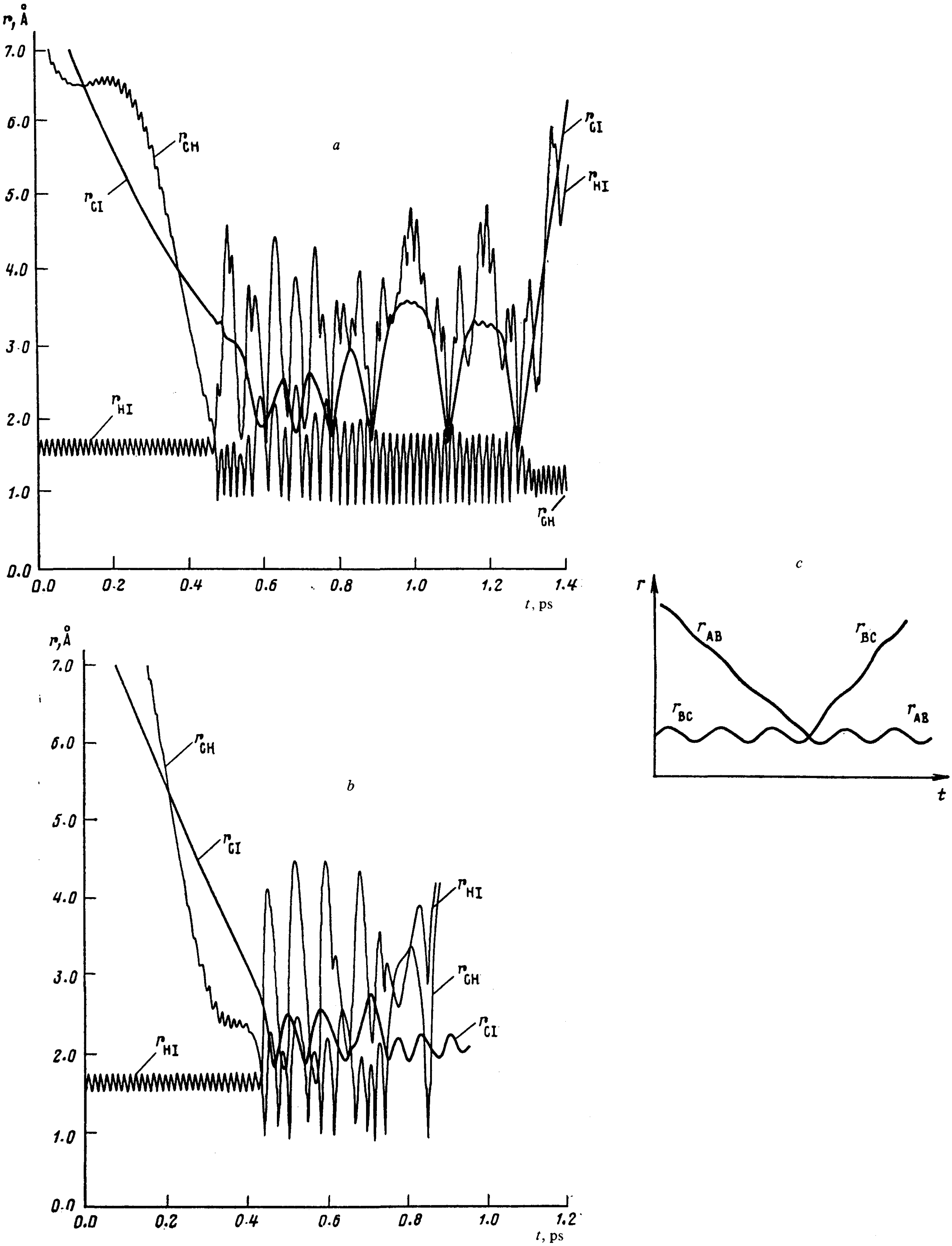


Figure 7. Examples of reaction trajectories: *a*) for $C(^1D)$ + HI → CH + I; *b*) for $C(^1D)$ + HI → CI + H; *c*) generalised trajectory for the forward reaction A + BC → AB + C.

between different PES in regions where they approach one another or quasi-intersect, then arises. Such jumps distort the reaction trajectories and allowance for them constitutes a serious problem in chemical dynamics.

In trajectory dynamics, account is taken of many trajectories for a given reaction (by no means all cross the bridge between the reactants valley and the products valley), and then the overall reaction cross-section in the specified states of the reactants is obtained by averaging the results with respect to the initial (starting) conditions governing the trajectories; one of the popular methods of selecting the initial conditions (but not the only one) is the Monte Carlo method.

Dynamic trajectory calculations yield the most complete information about the chemical reaction and provide answers to the following questions: what reaction channels exist, what are their probabilities, how is the energy of the reactants utilised in the reaction, how is it redistributed in the products, and at which modes of the motion is it localised. However, they are laborious and are by no means always fully realisable, being used predominantly for the simplest reactions. Simpler versions of the theory are therefore being developed, among which the method of the reaction pathway Hamiltonian merits special attention.

In this version of the theory, the classical Hamiltonian of the molecular reaction system is constructed and the reaction pathway as well as orthogonal oscillations (deviations from the reaction pathway in the closest regions of the PES along the pathway) are found. In principle, this approach makes it possible to carry out calculations for polyatomic systems and has definite practical advantages: the entire PES is not needed, only a small proportion of the latter being required (the region corresponding to the valley on the reaction pathway), but these advantages entail the sacrifice of the physical rigour and completeness of the calculation.

Together with dynamic trajectory theories, statistical theories are also being developed in chemical dynamics. They are suitable for reactions proceeding via a long-lived intermediate complex (resembling those which can be seen on the trajectories in Figs.7*a* and 7*b*). The formation of the complex and its decomposition are then independent events. If during the lifetime of the complex τ_c, a statistical distribution of the energy takes place (subject to the conservation of the energy and the momentum), then the reaction complex can be treated as a statistical system and its behaviour can be described in terms of statistical laws.

The criterion which determines whether the reaction can be described by the statistical theory is not always definite; it is frequently assumed to be represented by the condition $\tau_c \gg \tau_{rot}, \tau_{vib}$, i.e. the lifetime of the complex is longer than the rotational and vibrational relaxation times. However, this condition is not unambiguous and statistical theories are frequently applicable even if this condition is not fulfilled and, conversely, they are not applicable when it is fulfilled. In order to predict the properties of the reaction complex, it is important to know the behaviour of van der Waals molecules (Section II), while information derivable from energy dynamics is important for the prediction of its "statistical nature" (Section IV).

The transition state theory is frequently included among statistical theories; strictly speaking, this is not correct, because the configuration of the atoms at the top of the crossing ridge (it is referred to as the transition state or the activated complex) decomposes only via the direct channel and is not a statistical system. This is associated with the fact that one degree of freedom, corresponding to the reaction coordinate, has been differentiated in the method itself (in its physical aspect) and, by definition, it is isolated from the other degrees of freedom of the reaction system. On the other hand, in the transition state theory an equilibrium distribution is adopted, but it is a consequence of the equilibrium nature of the initial reactants. In other words, it leads to the activated complex together with the reactants but is not created in it and in this sense the claim that the transition state theory belongs to the class of statistical theories can be regarded as correct.

In the transition state theory, there is no dynamics of motion along the PES, only the knowledge of the energy spectrum of the reaction system moving along the PES being required. During its long history, the theory has received new formulations and justifications and many versions of this theory have been created: the canonic theory [calculation of the rate constants $k(T)$], the microcanonic theory [calculation of the cross-sections $\sigma(E)$], the variational theory (ensuring allowance for only the one-way reaction trajectories), the adiabatic transition state theory (it takes into account the quantum-mechanical partition functions and tunnel corrections), and, finally, the variational quantum-mechanical (or generalised) theory.

At the present time the transition state theories are the most productive, although they are more in the nature of recipes and not all their approximations are reliable. It has been demonstrated for a large number of collinear reactions over a wide temperature range that the rate constants usually agree with the quantum-mechanical calculations and with experiment to within an error not greater than 30%, although there are instances where the discrepancies in the constants amount to a factor of several tens and hundreds and it is not possible to estimate *a priori* this artibrary aspect.

The question when does the description of the reaction require dynamic trajectory calculations and when are statistical theories sufficient is a problem in statistical and non-statistical, selective chemistry. It is important especially in the chemistry of highly excited states; the emphasis laid on this problem is a tribute to technical progress. Hence follows the sharp increase of interest in ergodic systems. Chemical dynamics is beginning to adopt on a wide scale the approaches based on the ideas of the ergodic hypothesis, theories of order and chaos in chemical reaction systems are being developed, and problems of the chemical dynamics of periodic, oscillating reactions are being discussed. The endeavour to move outside the framework of adiabatic models and to develop effective methods whereby non-adiabatic conditions can be taken into account is associated with these factors.

The chemical dynamics of reactions in the condensed phase adds a new problem to all the difficulties and problems of gas-phase dynamics—that of allowing for the influence of the medium whose molecules act on the atomic-molecular reaction systems and are, strictly speaking, participants in the reaction and the question to what number of participants can the treatment be restricted has no definite answer. The first attempt to solve this problem arose in the familiar Kramers theory based on the solution of the equation of diffusional motion along the reaction coordinate. This theory introduced the concept of friction along the reaction pathway and was later developed in different versions—on the basis of the Fokker–Planck equation in terms of various approximations (Kramers himself obtained his initial equation in terms of the Stokes–Smoluchowski approximation—see Section III) and then on the basis of the Langevin equations. It was shown that the Kramers theory can also be obtained from the simple Langevin equation, i.e. subject to the condition that the random force acting from the direction of the molecules of the medium on the reaction system moving along the reaction coordinate is described by a Markov process. The generalised Kramers theory can be obtained from the generalised

Langevin equation and is equivalent to the problem of the attainment of the apex of a one-dimensional potential barrier by a Brownian particle when the random force is described by a non-Markov stationary Gaussian process. The generalised Kramers theory is then equivalent to the generalised transition state theory. The physical significance of the analogies is clear—the molecules of the medium (thermostat) act as a perturbing trajectory of the motion of the reaction medium along the reaction coordinate. The prospects for the development of a theory based on the quantum-mechanical version of the generalised Langevin equation have also been considered, but this is a difficult problem requiring the knowledge of the nature of the thermostat and of the details of the interaction of the reaction system with the thermostat at the quantum-mechanical level.

There have been definite advances in the development of theories of charge transfer reactions; they are based on the idea of the reorganisation of the medium as a result of fluctuations in dielectric polarisation. Such reorganisation produces potential wells and barriers, i.e. produces a potential surface, and this process is described by the classical theory, while movement along the reaction coordinate can be described within the framework of any dynamic theory (in particular, a purely tunnel version can be considered for electron transfer). A generalised quantum-mechanical-classical theory, in which the classical treatment of the movement of nuclei is combined with the quantum-mechanical description of the movement of electrons is also being developed.

The state of the theory of chemical reactions in the condensed phase is such that the theory and experiment are developing almost independently; the theory predicts merely general qualitative features but is incapable of making quantitative predictions. The difficulties are associated with the fact that many important details of the physics of the reactions are obscure—it is not clear what is the main factor which needs to be taken into account and what is of secondary importance and negligible in the theory.

2. Energetics in Reaction Dynamics

This problem has two aspects. The first involves the question of how the reacting molecules utilise the energy supplied to them, what energy is most effective and for what reactions, and under what conditions do the molecules employ their energy with the maximum benefit for the reaction. These questions have a direct bearing on the selective pumping of the energy to the degrees of freedom responsible for movement along the reaction coordinate—the control and stimulation of selected reactions. The second aspect involves the questions how energy is liberated in the chemical reaction, where it proceeds, where and in what forms it is localised, and how can it be concentrated and utilised. These questions have a bearing on the creation of laser media and effective pumping procedures in chemical lasers.

In principle, the answers to the majority of these questions are provided by trajectory calculations, but the laborious nature of the calculations and the limited accessibility of the PES has stimulated an alternative, experimental procedure, involving the use of modern laser spectroscopy, which makes it possible to produce and detect molecules in any quantum-mechanical states.

We shall deal first with the first set of questions—the ways of controlling reactions by pumping energy to the reacting species. These questions have no general answer; it depends on the type and topology of the PES, on the type of reaction, on the value of the energy, and on the type of the energy reservoir—*E*, *V*, *R*, or *T*.

When the electron reservoir is pumped up, electronically excited states are created, but even they exhibit a selectivity in reactions: each type of reaction is stimulated only by an electronic excitation of a definite type. The pumping of energy into the electron shell by no means stimulate every reaction despite the enormous amount of energy stored. One of the problems is to discover the nature of the selectivity, to learn how to predict it, and to employ it economically in the photostimulation, radiation-stimulation, and plasma-stimulation of processes.

The question of the relative contributions of the kinetic and vibrational energies to the activation of reactions is important. Thus, for reactions with a large barrier, there exists a kinetic energy threshold above which the reaction cross-section increases to a maximum and then diminishes. For endothermic reactions, the vibrational energy is much more effective than the kinetic energy, while for exothermic reactions the opposite situation obtains. The vibrational pumping of molecules is of special interest for two reasons: the vibrational energy relaxes with difficulty (at any rate much less easily than the kinetic and rotational energies) and should therefore be retained for a long time in the vibrational modes; the availability of powerful lasers operating in the vibrational-frequency range makes the question of practical significance.

The efficiency of vibrational energy in reactions depends on the heat of reaction, on the topology of the PES, on the height of the barrier, on the size of the vibrational quantum, on the adiabatic conditions, on the type of reactions (transfer of an atom, metathesis), on the complexity of the molecules, on the density of the vibrational states, on whether the reaction is of the direct, single-step type, or whether it proceeds via an intermediate statistical complex. Only one important feature has been reliably established and justified theoretically: the vibrational excitation is effective in overcoming the endothermic component of the potential barrier and hardly influences the overcoming of the barrier in thermally neutral and exothermic reactions. Its origin is inherent in the topology of the PES: for endothermic reactions, the barrier is encountered at an "early" stage, being displaced towards the initial reactants valley, while for exothermic reactions the barrier occurs at a "late" stage, being displaced towards the products valley.

For example, the reactions $Ca(Sr) + HF \rightarrow CaF(SrF) + H$ are accelerated by a factor of 10^4 already by the first vibrational quantum absorbed by HF, while the reaction $F + HCl \rightarrow HF + Cl$ with vibrationally excited HCl ($\nu = 1$) is accelerated only by a factor of 4. The reaction $CH_3 + H_2 \rightarrow CH_4 + H$ with participation of $H_2(\nu)$ is accelerated, while the excitation of CH_3 can accelerate, suppress, or altogether fail to influence the reaction, depending on the type of vibration excited. In the reaction $K + HCl \rightarrow KCl + H$, $HCl(\nu = 1)$ molecules react 100 times faster than $HCl(\nu = 0)$ and only 10 times faster if the same amount of energy is "thrown" into the kinetic degrees of freedom. In the reaction $OH + H_2 \rightarrow H_2O + H$, the $H_2(\nu = 1)$ molecules react 150 times faster than $H_2(\nu = 0)$, but the acceleration in the pumping of OH to the $\nu = 1$ state is only by a factor of 1.3. Neither the pumping of OH nor the pumping of CO alters significantly the rate of the reaction $OH + CO \rightarrow CO_2 + H$, while the reaction $O_2 + CN \rightarrow CO_2 + N$ is actually retarded by the pumping. The excitation of the HCO vibrations inhibits the HCO + NO reaction and this is evidence that it proceeds via a statistical complex.

An enormous number of such facts and observations exist for gas-phase reactions and by no means all have been explained satisfactorily. In the condensed phase the problem in activation is complicated by the rapid vibrational relaxation (see Section IV). There are very few data for reactions on solid surfaces (for example, it is known that the reaction $N_2O + Cu \rightarrow CuO + N_2$ is accelerated by a factor of 10^3-10^4 when vibrationally excited N_2O molecules participate in it), but this field will develop vigorously.

The influence of rotational pumping on reactions has been investigated mainly by the method involving the selection of rotational states in quadrupolar fields and by laser methods. The rate constants $k(J)$ for the reactions $Na + HF \rightarrow NaF + H$ and $Na + HCl \rightarrow NaCl + H$ decrease with increase in the rotational quantum number J to $J_{min} = 11$ (for the first reaction) and 7 (for the second), and then increase with increase in $J > J_{min}$. The reaction $K + RbF \rightarrow KF + Rb$ is exothermic, $k(J)$ falling with increased J; the reaction $H + OH \rightarrow H_2 + O(^1D)$ is also exothermic, but $k(J)$ increases with increased J. The rotation of OH accelerates the reaction $NO + OH \rightarrow NO_2 + H$, while the rotation of NO accelerates the reaction $NO + O_3 \rightarrow NO_2 + O_2$. In the reaction $H + HBr \rightarrow HBr + H$ with $v = 0$, J does not influence the reaction, but, when $v = 2$, the constant $k(J)$ increases with increasing J, i.e. the effect of the rotational R-energy depends on the vibrational state. The reaction $Br + HBr \rightarrow HBr + Br$ with HBr ($v = 0$) is insensitive to J up to $J \leq 10$, but is accelerated sharply for $J > 10$.

The influence of the R-energy depends on the kinetic energy: for a high kinetic energy (above the threshold), the influence of the R-energy is insignificant, which is understandable: for high rates, the time of contact between the species is much shorter than the period of the rotation and the rotational state of the reactant becomes insignificant for the reaction. The inhibition of the reaction by rotation, i.e. the decrease of $k(J)$ with increase of J, is also understandable to a first approximation: the reaction requires a definite orientation of the reactants, an appropriate orientation throughout the contact time, while rotation disrupts this arrangement. This is the effect involving the gyroscopic stabilisation of molecules: a rapidly rotating molecule averages out the perturbing potential of the incoming partner and this "saves it" from reaction.

However, these are only the few features which are understandable; much remains obscure and difficult to predict. The principal factor is apparently the ratio of the angular velocity of the rotating molecule to the relative velocity of the movement of the partners—it determines the efficiency of the R-energy in the reaction and so far there is no general solution to this problem.

An attractive problem involves the search for non-traditional and sometimes non-evident methods of controlling reactions using energetically weak influences. This is possible in systems with degenerate states, which, however, differ in reactivity. Then even weak influences induce almost isoenergetic transitions from one less reactive state to another, more reactive state. This is in fact the principle of magnetic influences on chemical reactions (see Section VI); this is also possible in laser chemistry, where the direction of the reaction can be altered by weak coherent radiation.

The idea can be illustrated by an example: suppose that the molecule decomposes into different products for a certain energy, which means that it possesses a series of degenerate continuous states, each of which is correlated with a definite composition of the products. The key question is how to intensify the selectivity of the molecules in relation to these states—how to achieve their selective population. This requires the control of the composition by a coherent linear superposition of these degenerate states. It can be achieved if the initial molecule is prepared by coherent irradiation with superposition of bound states and is then dissociated in a specified state. This idea has been realised experimentally in the photolysis of CH_3I via two channels:

$$CH_3I \rightarrow CH_3 + I(^2P_{1/2})$$
$$CH_3I \rightarrow CH_3 + I(^2P_{3/2})\,.$$

Using two-frequency laser irradiation (one frequency for the superposition of the coherently bound states and the other for photodissociation via one or other channel), it is possible to increase by a factor of two the quantum yield of the decomposition for an unchanged energy expenditure and to alter the competition between the channels. This is in essence the first example where energetic coherence has been manifested in chemical reactions.

We shall now turn to the second range of questions, concerning the fate of the heat of reaction. A most attractive procedure is to convert the heat (when it is sufficient) into an "intensive" form of energy—electronic energy. The efficiency of the electronic pumping into the reaction product depends on many factors—the magnitude of the heat of reaction, the orbital and spin prohibitions, the quasi-intersections of the PES, and the non-adiabatic nature of the trajectories on the PES. For these reasons, the quantum yield of the electronic pumping in different reactions (usually determined from the chemiluminescence yield) varies by many orders of magnitude—from 10^{-11} to ~1. It is important to establish the characteristics of the electronic pumping for the prediction of laser effects. They are widely investigated in the flames of metal vapours in CO, N_2O, O_2, O_3, etc. atmospheres, in the reactions of alkali metal atoms with halogen molecules, in the recombination of the N, O, etc. atoms on surfaces, etc. The search for chemical laser systems is one of the most vigorously developing fields of chemical physics.

The vibrational pumping of products is determined also by the topology of the PES: if there is an attractive potential between the reactants and the ridge separating the valleys occurs at an "early" stage, i.e. is displaced towards the reactants valley, the kinetic energy of the reactants is converted preferentially into the vibrational energy (V-energy) of the products; for a repulsive potential and a "late" ridge, the energy liberated remains in the kinetic form. Adiabatic conditions with respect to both ΔV and ΔR are frequently retained, i.e. the vibrational and rotational energies of the initial reactants are fully retained in the products. General characteristics have been scarcely established in this field hitherto, the adiabatic (or non-adiabatic) conditions, depending on the energy stored, the topology of the PES, and the vibrational-rotational coupling. For example, in the reaction $Cl + HD \rightarrow HCl + D$, the rotational energy is retained, while in the similar reaction $Cl + HD \rightarrow DCl + H$, the rotational energy of the initial molecule is converted almost fully into the kinetic energy of the products.

The energy pumping of the product frequently serves as the criterion of the reaction mechanism. Thus the reaction $Cs(7P_{1/2,\,3/2}) + H_2 \rightarrow CsH + H$ proceeds via the harpoon mechanism: the optical electron of the excited Cs atom is thrown like a harpoon from Cs to H_2 over long distances and the $Cs^+ + H_2^-$ ion pair is maintained as a result of the Coulombic potential and decomposes slowly into CsH and H. This mechanism agrees with the dynamic trajectory analysis of the PES on which the ionic and covalent energy levels "intersect". An important consequence of this mechanism is the strong rotational excitation of CsH: J_{max} reaches 17 and the maximum pumping has been achieved for $J = 10-12$.

The photolysis of H_2S in the gas phase at 193 nm leads to the formation of an H atom with an HS radical in the $^2\Pi_{3/2}$ or $^2\Pi_{1/2}$ states, their ratio being 3.75, which corresponds to an electronic temperature of 410 K. Vibrational excitation is almost completely absent and the rotational temperatures of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states are 375 and 220 K, i.e. the electronic and rotational temperatures are close to the temperature of the photolysis, which means that the energy of the photolysing quantum is converted into the kinetic energy and the decomposition takes place non-statistically. The opposite case is represented by the decomposition reaction $CF_3NO \rightarrow CF_3 + NO$. The distribution of CF_3 and NO with respect to v is nearly statistical and the rotational temperature of NO ($^2\Pi_{1/2}$) is 900 K and is very close to the statistical limit of 1025 K; the *V*- and *R*-energies of CF_3 and NO are close to this limit. The times corresponding to the appearance of CF_3 and NO at 670, 640, and 500 nm are 18.5, 8.8, and 4.3 ns and agree with the lifetimes of the "energised" CF_3NO molecules measured independently. Clearly, CF_3NO decomposes via a long-lived statistical complex.

The present experimental level of research into pathways leading to energy pumping is demonstrated by the analysis of the energy states of the products in the following reactions:

$H+O_2 \rightarrow OH+O; \quad \Delta H = 16.6 \text{ kcal mol}^{-1};$
$H+CO_2 \rightarrow OH+CO; \quad \Delta H = 25.4 \text{ kcal mol}^{-1};$
$H+H_2O \rightarrow OH+H_2; \quad \Delta H = 14.8 \text{ kcal mol}^{-1}.$

All these reactions are endothermic, but the H atoms generated by the photolysis of HI are hot and the energy of the collision of H with its reaction partners (O_2, CO_2, H_2O) is 60 kcal mol^{-1}, which greatly exceeds the endothermicity. Despite the high collision energy in the $H + CO_2$ and $H + H_2O$ reactions, there is no vibrational excitation of OH (there are none in states with $v = 1$), but in the $H + O_2$ reaction there is significant vibrational pumping: the population of OH ($v = 1$) is only a factor of 2 smaller than the population of OH ($v = 0$).

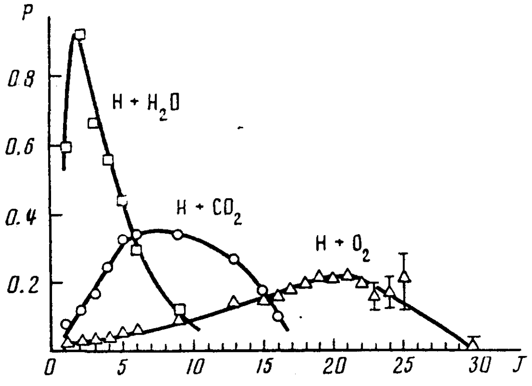


Figure 8. The populations *P* (in relative units) of the rotational states of OH ($v = 0$) in the reactions of a hydrogen atom with H_2O CO_2, and O_2 (pressure 0.2 mmHg, probing pulse delay time 100 ns).

The rotational excitation of OH in the $H + O_2$ reaction is very hot (*J* is large—Fig.8), while in the $H + H_2O$ reaction it is virtually absent, although the energetics are the same. In the $H + H_2O$ reaction the rotational distribution does not correspond to the statistical distribution, while in the $H + O_2$ reaction the statistical distribution obtains but this does not mean that the reaction can be treated statistically. This agreement is fotuitous: trajectory calculations have shown that the transition complex HO_2 on the non-empirical PES in the vicinity of the ridge has a lifetime of ~0.1 ps and the distribution of the rotational energy agrees with the experimental distribution in the absence of statistical equilibrium.

The spin-orbit doublets $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ are populated statistically, but the population of the Π^+ component of the Λ doublet takes place preferentially in all three reactions by a factor of 3–6. This means that an angular momentum is generated in all the reactions in the plane containing the bond undergoing dissociation, i.e. that the output channel in these reactions lies in a single plane. Otherwise, an angular momentum would have been created in the reaction around the bond being dissociated and this would have entailed the preferential population of the Π-component of the Λ doublet.

These features of the dynamics and energetics of all three reactions presented are associated with the characteristics of their PES and indicate how effectively the PES "conducts" both the chemical and energy dynamics.

3. Chemical Kinetics and Reaction Mechanisms

Chemical kinetics as the science of process rates and mechanisms is part of reaction dynamics; it has long outgrown their traditional framework and has reached a new level. Formal kinetics has been converted into a routine technique, the new level of modern kinetics being determined by the wide-scale application of a wide variety of physical methods permitting the reliable identification of the majority of intermediate species with a high time resolution (down to tens of femtoseconds). Reliable methods, characteristics, and criteria have been developed, whereby it is possible to achieve a sufficiently full determination of any mechanism.

The knowledge of the mechanism is not the ultimate aim; it is necessary to determine the rate-limiting stage, to establish the main and secondary pathways, and to select the method of controlling the process in order to increase its productivity and selectivity. The knowledge of the mechanism is the most important element on the way to creating intensive highly selective and energy saving chemical technologies.

A considerable proportion of chemical physics is devoted to kinetic studies and chemical mechanisms. It is concerned with the mechanisms of the reactions in molecular beams, ion-molecule reactions, the reactions of excited species, oxidation-reduction reactions, metal complex, acid–base, heterogeneous, micellar, and enzyme catalysis, and electrochemical reactions. Priority has been given to catalytic processes, plasma chemistry, combustion processes, reactions in solids, and processes associated with chemical energetics (new current sources, chemical methods for the accumulation and transformation of energy, etc.). Among them, we may mention the creation of new combustion regimes—the solid-phase oxygen-free combustion (self-propagating high-temperature synthesis), the creation of a "superadiabatic" regime with extremely high effeciencies approaching 100%, and combustion coupled with energy consuming processes. In the chemical physics of solid-phase reactions, valuable low-temperature chemical "explosions", induced by the mechanical stresses in strongly cooled glasses, and the quantum-mechanical limits of the rates of low-temperature reactions have been discovered and new types of mechanochemical processes, induced by shear deformation at high pressures and by shock waves, have been observed. There has been a sharp growth of interest in the problem of the macroscopic storage of mechanical energy and the utilisation of this store for the activation of chemical processes is a tentative basis of promising technologies.

A remarkable property of chemical reactions in solids has been established—even in the kinetic regime the reactions are controlled by the molecular dynamics of the solid so that the molecular organisation of the transition state and not the chemical step proper becomes the rate-limiting stage. This alters, in principle, the concept of the reactivity of species in a solid and leads to new ways of controlling reactions via the physics and mechanics of the solid.

VI. SPIN DYNAMICS

Spin dynamics includes the dynamics of the populations of the spin states of atomic-molecular species and matter, the dynamics and mechanisms of the pumping and relaxation of spin states, and the dynamics of the change of the angular momentum. It can be subdivided into two components—spin dynamics in systems without a chemical reaction and spin dynamics in reactive systems.

The first component is the traditional field adjoining magnetic resonances and magnetic resonance spectroscopy as a method in chemical physics. It includes an enormous number of problems—magnetic relaxation of electrons and nuclei, the dynamics of spin systems in UHF and microwave frequency fields, the exchange of magnetic energy between the Zeeman and magnetic-dipolar reservoirs, joint electronic-nuclear relaxation and the orientation of nuclei (dynamic nuclear polarisation), electron–electron relaxation and electron–electron double resonance, spin–orbit coupling and its contribution to the spin dynamics, and the spin relaxation and transition between the spin states of triplet moelcules, ions, carbenes, metal complexes, clusters, etc. A special branch of spin dynamics is associated with the optical orientation of electrons and nuclei: these phenomena are known in gases, in plasma, in molecular crystals, in impurity centres of a solid, and recently also in liquids.

Spin dynamics is controlled by magnetic perturbations and their time variation, being determined by the amplitude of the perturbation and the duration of its action and it therefore carries simultaneously information both about the structure and about the dynamics of the perturbations (molecular or chemical information). This is important for magnetic microwave spectroscopy as a physical method for structural analysis and for the identification of chemical species and substances and also for magnetometry (including quantum-mechanical magnetometry).

However, spin dynamics can be sensitive also to non-magnetic, purely electrostatic interactions. For example, the rate of singlet–triplet conversion in the carbene Ph_2C depends on the polarity of the solvent. This is possible owing to the Coulombic polarisation of the electron shell (on complex formation, solvation, etc.); this effect can alter the contribution of the spin–orbit coupling to the spin relaxation and can alter the spin dynamics. Another example: the electron-spin relaxation of the Na, K, Rb, and Cs atoms in the inversely populated state $^2S_{1/2}$ depends greatly on the nature of the "buffer" gas (He, Ne, H_2, CH_4, NH_3, C_6H_6, etc.). The cause of the effect is as follows: in the impact of an atom against the buffer molecule, Coulombic forces induce an orbital moment, while the spin–orbital coupling induces in its trun spin relaxation. Here not only the rate of relaxation but also the extent of the hyperfine magnetic interaction of the electron with its nucleus in the metal atom depends on the nature of the buffer gas. Thus highly polar molecules diminish the hyperfine interaction constant, because, in strong collisions between an atom and such molecules, the electron shell of the atom is polarised and a *p* orbital with a zero-point hyperfine interaction becomes mixed with the spherically symmetrical *s* orbital.

The dynamics of the exchange of the angular momenta (orbital and spin) between the molecules play a significant role in many processes, including the functioning of lasers. For example, in the iodine laser with emission based on the transition $I(5^2P_{1/2}) \rightarrow I(5^2P_{3/2}) + h\nu$, the inverse population is restored in the process $I(5^2P_{3/2}) + O_2(^1\Delta g) \rightarrow I(5^2P_{1/2}) + O_2(^3\Sigma_g^-)$, i.e. the electron-spin momentum is transferred from oxygen to the angular momentum of the iodine atom.

The spin dynamics in chemically reacting systems ensures an even greater richness of phenomena. In chemical reactions prohibitions based on the angular momentum (both orbital and, especially, spin momentum) are very strong, i.e. reactions requiring a change in the angular momentum are strictly prohibited; only reactions which are not accompanied by a change in momentum are allowed. The evidence for this postulate is numerous and reliable. Thus molecular, ion-molecule, and even radical substitution and addition reactions in solutions are not accompanied by the polarisation of the nuclear spins, which is a feature of the change in the electron spin. Even in reactions with participation of atoms with strong spin–orbit coupling, the spin is retained:

$$F(^2P_{1/2}) + Br_2 \rightarrow FBr + Br(^2P_{1/2})$$
$$F(^2P_{3/2}) + Br_2 \rightarrow FBr + Br(^2P_{3/2})$$
$$Br(^2P_{3/2}) + IBr \rightarrow Br_2 + I(^2P_{3/2})$$

(these reactions are significant in gas lasers based on halogen atoms).

The rigour with which the spin is retained and the rigour of the spin prohibitions of chemical reactions are evident from simple physical considerations alone. The intrinsic time of the elementary reaction is a fraction of a picosecond and magnetic or spin–orbit perturbations exerting an enormous force are necessary to alter the spin during this period. As a rule, such high-energy perturbations do not occur in the transition states of reactions. For this reason, spin is conserved in the vast majority of chemical reactions. Exceptions may be expected only in rare cases [for example, in reactions with a long-lived statistical complex (see Section V)]. The spin prohibitions in chemical reactions are stronger than the energy prohibitions: the latter are statistical in character (an energy fluctuation sufficient to overcome the barrier can always occur), while the former are absolute.

The existence of spin prohibitions has long been suspected, but their importance and scale have been estimated only recently and their consequences observed—magnetic effects in chemical reactions: the influence of weak magnetic fields on photophysical and photochemical processes in molecular solids, the influence of magnetic fields on chemical reactions, the dependence of the reaction rates on the magnetic moments of the nuclei of the reactants (the magnetic isotope effect), chemically induced dynamic nuclear polarisation, the microwave frequency maser-chemical effect, chemically induced magnetic electron polarisation, and the influence of high-frequency electromagnetic fields on chemical reactions. The discovery of these effects is a striking illustration of the definition of creativity as a way of converting the unpredictable into the inevitable. Fairly soon after their discovery, these effects passed from the class of intriguing incomprehensible phenomena to the class of self-evident phenomena with a simple and clear physics.

In order to remove the spin prohibition, i.e. in order to alter the spin, long-acting magnetic perturbations are needed. An example of long-lived states with magnetic interactions is provided by a pair of two radicals in which two unpaired electrons can exist in two spin states—singlet or triplet. The generation of molecules from the singlet pair is spin-allowed, while the generation from the triplet pair is prohibited. The reaction in the triplet pair stops and "waits" until magnetic interactions (Zeeman, hyperfine, or dipolar) alter the spin pairing and cause its transition from the triplet to the singlet states. In this spin-prepared pair prohibition of the reaction has been removed and reaction restarts. Thus the source of magnetic effects is the spin selectivity of chemical reactions.

Long-lived states with magnetic interactions are realised in pairs with participation of radicals, triplet molecules, electrons, paramagnetic holes, ions, and solitons—all are species with unpaired electrons. Magnetic interactions induce in these pairs transitions between various spin states and remove the prohibition of spin-selective chemical reactions in such pairs. Magnetic effects are therefore observed in varied processes—photoconductivity and photoluminescence, dark conductivity of organic semiconductors, the annihilation of broken bonds in mechanically deformed inorganic semiconductors, photosynthesis, changes in the rates of chemical reactions and product yields, etc.

Magnetic perturbations in pairs, which removes the spin prohibition, depend on the external magnetic field and are a source of magnetic field effects. They also depend on the magnetic electronic-nuclear interaction, on the magnetic moment of the nuclei, and on the magnetic spin and its projection—a dependence which leads to the magnetic isotope effect and to chemically induced nuclear polarisation. When the polarisation of the nuclei is high (and it can reach record values in the range 10^4–10^6 which are unobtainable in physics) and exceeds the generation threshold, the movement of the nuclear spins becomes coherent and a new property of chemical reactions is observed—the ability to generate a microwave frequency field, i.e. the chemical reaction becomes a kind of molecular quantum generator with chemical pumping—a chemical maser.

The spin state of the pairs and hence their reactivity can also be altered by the action of high-frequency fields. This leads to new possibilities for controlling chemical reactions and for developing new magnetic resonance methods; appreciable advances have already been made on these lines.

Quantum beats have been observed in the triplet–singlet conversion in the pairs and hence in the reactivity of these pairs and in the yields of the chemical products of their reactions. Ways of controlling the coherence of the spin dynamics of pairs with the aid of high-frequency fields have been found; this is the second example where coherence "operates" in chemistry (for the first, see Section V).

We may note a difference between the spin and magnetic effects. Spin effects, i.e. spin prohibitions, exist in all the states of matter—gases, liquids, solids, and plasma. However, in gases and plasma the duration of contact between the species is 10^{-13}–10^{-14} s and is too short for the occurrence of the magnetically induced spin conversion of the pairs. Only in liquids and solids are the spin effects accompanied by magnetic effects, since only under these conditions is the lifetime of the pairs of reacting species comparable to the spin evolution time and magnetic forces act for a sufficiently long time to alter the spin.

The spin evolution of pairs is induced via two channels. The "useful" channel includes evolution as a result of the Zeeman and hyperfine interactions and leads to all the magnetic effects enumerated above. The second channel includes the spin evolution induced by the dipolar interaction of the electrons and the spin–orbit coupling. It depends little on the magnetic field and involves the nuclear-spin system to only a slight extent and for this reason it makes possible the "leakage" of the spin states, lowers the scale of the magnetic effects and in this sense it is "harmful" and difficult to control.

Control of spin dynamics is one of the important problems of chemical physics: the scale of the magnetic effects depends on it. Thus the magnetic isotope effect and the efficiency of the separation of magnetic and non-magnetic isotopes in chemical reactions are determined by the spin, molecular, and chemical dynamics. In other words, they depend on the spin evolution and the competing processes involving the dissociation of pairs into isolated species (molecular dynamics) and the chemical reaction of the pairs, which restrict the spin evolution time. However, the problem is not only that of creating favourable "physical" conditions for spin evolution (adequate magnetic interactions, optimum lifetimes of the pairs, favourable molecular dynamics, minimum "leakage" via the harmful channel) but it is also necessary to "organise" chemistry and chemical reactions with respect to the specified physics (to create the required pairs with an intense Zeeman or hyperfine interaction, to specify a favourable starting spin state of the pairs, and to drive the reactions via the specified pathway). Clearly the problems of controlling spin dynamics are the problems of controlling the physics and chemistry of reactions.

Spin dynamics has two remarkable advantages: the first is that it reliably controls chemical reactions in the pairs and in its turn is itself controlled by weak magnetic interactions with negligibly small energies. This factor leads to non-traditional ways of controlling many physicochemical processes with the aid of weak magnetic and electromagnetic influences.

Pairs of spin-containing species, in which long-acting magnetic perturbations operate, altering the spin state of such pairs, are not the only type of magnetosensitive systems. Another type comprises electronically excited molecules or ions in which there is a set of energy states with different spin multiplicities. During the lifetime of these excited molecules, magnetically induced conversion takes place between these energy states, including conversion to predissociation levels at which the molecules decompose. This leads to a dependence of the luminescence and the decomposition of the molecules on the magnetic field. Effects of this type have been observed in the gas phase (where the lifetime of the excited molecules are sufficiently long) and they constitute one of the new fields in the chemical physics of gas-phase reactions.

VII. CONCLUSION

A reader with a rigorous viewpoint will say that the limits of chemical physics outlined in this article have been enormously extended, and he is right: in by no means all the fields and problems mentioned here has a leading position been attributed to chemical physics. Many of them are being worked out and solved in related chemical sciences—physical and quantum chemistry, the chemistry of high energies, electrochemistry, photochemistry and radiation chemistry, biochemistry, the chemistry of high-molecular-weight compounds, etc. Chemical physics overlaps (and this is natural) with solid state physics, molecular physics, biophysics and, to an especially great extent, physical and quantum chemistry. However, when one is dealing with the physics of chemical processes, the physics in chemistry, then one is concerned with chemical physics—it is its characteristic feature and reliable criterion.

There is an interesting feature in the development of chemistry. The traditional chemical and chemical engineering fields, which constitute the basis of chemical industry (petrochemistry, the manufacture of fertilisers, fundamental organic synthesis, etc.) have been established and have developed almost independently of chemical physics. However, new fields (microelectronics, laser and plasma chemical technologies, modern catalysis, chemical lasers, modern chemical materials science, modern analysis and diagnostics, etc.) are firmly based on chemical physics and the development of future or predicted fields (such as molecular electtronics, the new generation of superconducting materials, chemical bionics, organic ferromagnetics, etc.) is altogether unthinkable without chemical physics.

The current emphasis, priorities, and growing points in chemical physics have been noted in various sections of the present article; they can be generalised and grouped around the following principal fields:

Physical principles governing the creation of new materials with new or extreme properties;

control of chemical processes and the development of chemical and physical principles of the control of reactivity and chemical dynamics—the "tuning" of reacting species to a specified reaction and a specified rate;

energy dynamics, the creation of new chemolasers and methods for the transformation and accumulation of chemical energy;

the principles of molecular organisation, chemical dynamics, and the functioning of molecularly organised systems as a basis of a new generation technology.

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The article represents a generalisation and a combination with the author's views and ideas of a large number of results, facts, ideas, and postulates described in numerous articles, communications, reviews, and books. The idea of this article arose in 1984 in connection with work on the analysis of the problems of modern chemistry (see V.A.Legasov and A.L.Buchachenko, Uspekhi Khimii, 1986, 55, 1949 Russ. Chem.Rev., 1986(12)), V.I.Gol'danskii, V.A.Legasov, and V.A.Benderskii for many useful, interesting, and inspiring discussions.

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Mössbauer Studies of Tunnel Phenomena in Chemical and Biological Physics

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The combination of various methods based on the use of the Mössbauer effect, namely the traditional Mössbauer absorption spectroscopy, Mössbauer emission spectroscopy, and the Rayleigh scattering of Mössbauer emission, has made it possible to observe a series of characteristic features of the kinetics of intramolecular oxidation-reduction processes (in relation to the conversion of Turnbull's blue into Prussian blue) and to investigate the dynamic properties of biopolymers over a wide range of temperatures and degrees of hydration.

A very important role of tunnel processes was discovered in both cases—the intramolecular tunnel electron transfer (electronic-nuclear tunnelling) and the phonon-stimulated tunnelling of atoms and atomic groups respectively.

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I. INTRODUCTION

A characteristic feature of the current employment of isotopes in various natural sciences is the fact that not only the radioactivity itself but also the properties of the radioactive decomposition (its rate and mechanism) and of the radiation emitted (energy and hyperfine spectra, absorption and scattering, angular correlations etc.) serve as sources of physicochemical information.

Many types of transformations of atomic nuclei and elementary particles are known (they are listed in Table 1), in which various effects of the atomic, molecular, and crystal environment are manifested and all the effects can be used to study this environment, especially its structural and dynamic properties.

Table 1. The transformations of atomic nuclei and elementary particles observed with the aid of radioisotopes and the effects of the atomic, molecular, and crystalline environments manifested in such observations.

Transformation	Effect
Electron capture	Changes in lifetime
Isomeric transitions (with internal electronic conversion)	Changes in conversion coefficients and lifetime
Mössbauer isomeric transitions	Changes in structural and dynamic parameters of Mössbauer spectra
Cascade transitions ($\gamma\gamma$, $\beta\gamma$, etc)	Perturbation of angular correlations
Emission of γ-rays or particles by polarised nuclei	Perturbation of the angular distribution of the emitted γ-rays or particles relative to the direction of spin
Annihilation of positrons	Changes in the lifetime of positrons and of the number and the angular and energy correlations of the annihilated γ-quanta

Two phenomena in the physics of atomic nuclear and elementary particles where the influence of the properties of the environment—the Mössbauer effect and the annihilation of slow positrons—are strikingly observed, have been particularly vigorously investigated by the Structure of Matter Division of the Institute of Chemical Physics at the USSR Academy of Sciences.[1-4] A wide range of our investigations has been devoted to the development and application of chemical Mössbauer spectroscopy (MS). We began with the most traditional method—Mössbauer absorption spectroscopy (MAS), but subsequently the range of methods employed was extended and included also Mössbauer emission spectroscopy (MES), the Mössbauer spectroscopy of conversion electrons (MSCE), and the Rayleigh scattering of the Mössbauer emission (RSME).

In the present review we shall consider the application of MES and RSME to the study of tunnel phenomena in chemical and biological physics, namely the intramolecular tunnel electron transfer and the phonon-stimulated tunnelling of atoms and atomic groups in biopolymers. Thus we proceed from two directions—we apply various Mössbauer methods (MES and RSME in combination with MAS), investigate various objects, sometimes widely differing in their nature, namely inorganic coordination compounds and bio-organic macromolecules. Nevertheless the results obtained are closely related and supplement one another; they all deepen and extend our understanding of tunnelling processes and thus fall within the general range of studies of the tunnel effect in chemistry, electronic-nuclear and molecular tunnelling, and the low-temperature quantum limit of the rates of chemical reactions.[5-8]

II. STUDIES OF THE INTRAMOLECULAR TUNNEL ELECTRON TRANSFER BY THE MES METHOD

We shall begin with the use of Mössbauer spectroscopy (MES and MAS) in the study of the spatial and time delocalisation of electrons in molecules or more complex systems.[9] It is evident that, if we are dealing with a system of two potential wells separated by a barrier (Fig.1), then the electronic levels located above this barrier belong to neither the left-hand nor to the right-hand well and describe the system as a whole. For the sub-barrier levels, the situation is more complex.

We shall consider, for example, the simplest case of the behaviour of the electron in two identical potential wells, where it occupies one of the sub-barrier levels. It can be seen that in this case one could assume that the electron is either in the left-hand well (wave function ψ_l) or in the right-hand well (wave function ψ_r). However, neither of these positions of the electron (i.e. its spatial localisation) corresponds to the eigenstate of such a system. The eigenstates are symmetric $\psi_s = (1/\sqrt{2})(\psi_l + \psi_r)$ or antisymmetric $\psi_a = (1/\sqrt{2})(\psi_l - \psi_r)$ combinations of the wave functions ψ_l and ψ_r with energies differing by $\Delta E_{as} = \hbar/\tau$.

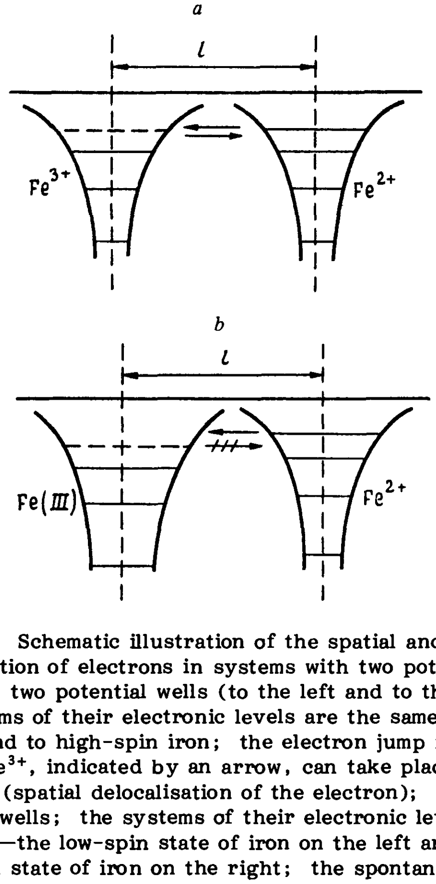

Figure 1. Schematic illustration of the spatial and time delocalisation of electrons in systems with two potential wells: *a*) two potential wells (to the left and to the right); the systems of their electronic levels are the same and correspond to high-spin iron; the electron jump from Fe^{2+} to Fe^{3+}, indicated by an arrow, can take place in either direction (spatial delocalisation of the electron); *b*) two potential wells; the systems of their electronic levels are different—the low-spin state of iron on the left and the high-spin state of iron on the right; the spontaneous electron transition from the upper level can take place only from right to left.

The energy splitting is thus related to the characteristic localisation time τ or, in other words, to the time required for the oscillation (jump) of the electron between the left-hand and right-hand wells. Only if the time τ is large compared with the characteristic time of the measurement by the given experimental method (τ_{exp}) is it possible to observe the spatial localisation of the states ψ_l and ψ_r.

For example, if the electron is in a system where two identical potential wells are represented by two high-spin tervalent iron ions Fe^{3+} (the ions *a* and *b*) then the wave function ψ_l will describe the Fe_a^{2+}–Fe_b^{3+} state, while the wave function ψ_r will describe the Fe_a^{3+}–Fe_b^{2+} state (Fig.1*a*). Each of these ions (*a* and *b*) spends 50% of time in the high-spin states of bivalent iron (Fe^{2+}) and tervalent iron (Fe^{3+}). The characteristic time of the measurement in Mössbauer spectroscopy is the average lifetime of the excited level $\tau_{exp} = \tau_M$, which is $\tau_M = 1.4 \times 10^{-7}$ s for ^{57}Fe. It the time taken for the electron jump between the two wells is greater than or comparable to the lifetime, $\tau \gtrsim \tau_M$, then two Mössbauer absorption spectra, representing both Fe^{2+} and Fe^{3+}, will be observed. If the jump time is much shorter than the time of the Mössbauer transition, $\tau \ll \tau_M$, only one Mössbauer spectrum, intermediate between those of Fe^{2+} and Fe^{3+}, will be observed. Thus MAS makes it possible not only to establish the very fact of the spatial delocalisation of electrons but also to investigate quantitatively the time scale characterising the electron jumps between different states.

The use of MES opens up new possibilities. Suppose that there are two different potential wells, for example, two tervalent iron ions, differing in their properties: we shall assume that one of them is in the high-spin (Fe^{3+}) state and the other is in the low-spin [Fe(III)] state (Fig.1*b*). In this case the presence of an additional electron in one of these potential wells is energetically more favourable than its presence in the other well and for this reason only one of the two possible states—the one with the lower energy—is represented in the usual (absorption) Mössbauer spectra.

However, we shall assume that at the instant of the formation of the Mössbauer nuclear level, the corresponding atom is in a higher, unstable electronic state of the system and that the system passes to a stable state only later, while the characteristic time of the transition is close to or greater than the lifetime of the Mössbauer level. In this case there is a possibility of noting the contribution of the initial unstable state of the system to the Mössbauer emission spectrum. This contribution may be especially significant for short time intervals immediately after the population of the Mössbauer level.

All these general considerations can be clearly illustrated in relation to compounds well known to chemists—the ferricyanide–ferrocyanide complexes called Prussian blue (PB) and Turnbull's blue (TB). The formation of these beautiful blue deposits is used to detect the high-spin Fe^{3+} or Fe^{2+} ions in solutions. The addition of potassium ferrocyanide $K_4[Fe^{II}(CN)_6]$, a salt of the low-spin bivalent iron, to Fe^{3+} salts causes the precipitation of PB, tentatively having the composition $Fe_4^{3+}[Fe^{II}(CN)_6]_3^{4-}$, while the addition of potassium ferricyanide $K_3[Fe^{III}(CN)_6]$. a salt of the low-spin tervalent iron, to Fe^{2+} salts leads to the formation of TB, which has the tentative composition $Fe_3^{2+}[Fe^{III}(CN)_6]_2^{3-}$.

All four forms of iron participating in these reactions—Fe^{3+}, Fe^{2+}, Fe(III), and Fe(II)—have different Mössbauer spectra (Fig.2); it is therefore not surprising that already in the very earliest stage of development of Mössbauer spectroscopy several laboratories in different countries (including our laboratory) began to investigate the absorption spectra of PB and TB in an attempt to identify both compounds. However, it was found that, whatever method used to prepare the compounds (Fig.2), only one resultant spectrum was always obtained, i.e. only one product, namely PB whose structure is illustrated in Fig.3, with low-spin bivalent iron Fe(II) ions adjoining carbon atoms, i.e. in an environment of ligands with a strong field, and high-spin tervalent iron (Fe^{3+}) ions adjoining nitrogen atoms, i.e. in an environment of ligands with a weak field; the additional Fe^{3+} ions occupy interstitial positions. The impression was created that TB does not exist at all and that the electron is always localised (in conformity with the situation illustrated in Fig.1*b*) at low-spin iron in all ferri-ferrocyanides.

The formation of precisely PB and not TB in all the procedures, listed above, for the preparation of iron cyanide complexes can be seen particularly clearly when the Mössbauer effect is used to analyse the position of the isotope label[10]—a method which is extremely convenient for the study of the structures, kinetics, and mechanisms of reactions of systems containing Mössbauer atoms in different functional states. In the instances described, the application of the Mössbauer effect involved the comparison of the absorption spectra with selective introduction of ^{57}Fe labels in the form of one of the four states of iron in one or both interacting compounds.[11]

Apart from the fact that the employment of the Mössbauer effect to analyse the state of the isotope labels confirmed the formation of Prussian blue and not Turnbull's blue in all the instances investigated, it also demonstrated that the sequence of the formation of the soluble and insoluble ferri-ferrocyanides differs significantly from, and sometimes is even completely opposed to, that adopted in the literature and that isotope exchange took place in solutions between different states of iron. However, these problems will not be discussed here and we shall proceed to experiments on Mössbauer emission spectroscopy (MES).

MES characterises the structural and dynamic properties of compounds containing emitters of resonance γ-quanta, i.e. atoms or nuclei in the highest excited Mössbauer level. The possibilities for the study of relaxation changes in such compounds are determined by the ratio of the lifetime of the Mössbauer level τ_M to the characteristic relaxation time τ_r. When $\tau_r \ll \tau_M$, relaxation takes place mainly before the nuclear transition and the emission spectra integrated with respect to time (IMES) therefore reflect principally the properties of emitters which have not undergone relaxation.

Nevertheless the use of delayed coincidences schemes with resolution time $\tau_{\text{coinc}} < \tau_M$, i.e. the study of the emission spectra differentiated with respect to time (DMES), leads to additional possibilities for the investigation of rapid relaxation processes. When $\tau_r \gg \tau_M$, predominantly atoms with unexcited nuclei, in the ground state, participate in the relaxation process and MES does not therefore carry any additional information.

Consequently the most favourable condition for the application of MES in its simplest (IMES) version is $\tau_r \sim \tau_M$. The usual values of τ_M are in the range 10^{-5}–10^{-10} s, while for ^{57}Fe (14.4 keV) we have $\tau_M \cong 1.4 \times 10^{-7}$ s and the emission of the resonance γ-quantum is in this case preceded by *K*-capture in ^{57}Co with formation of a short-lived ($\tau_0 \cong$ 12.5 ns) 136.4 keV excited state of ^{57}Fe and the subsequent emission of a non-Mössbauer 122 keV γ-quantum (Fig.4).

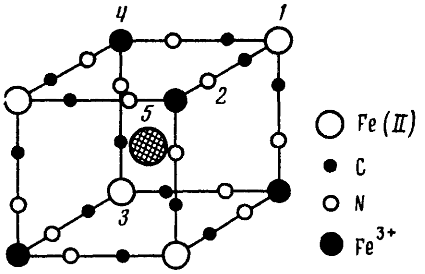

Figure 3. The structures of ferric ferrocyanides: *1*) C atom; *2*) N atom; *3*) low-spin iron atom at a lattice site; *4*) high-spin iron atom at a lattice site; *5*) high-spin iron atom in an interstitial position.

Thus the use of delayed ν (122 keV) and γ (14.4 keV) coincidences with a variable delay time (DMES) leads to the possibility of investigating relaxations with characteristic times ranging from $\tau_r \sim \tau_{\text{coinc}} \sim 10^{-9}$ s to $\tau_r \gtrsim \tau_M \cong 10^{-7}$ s.

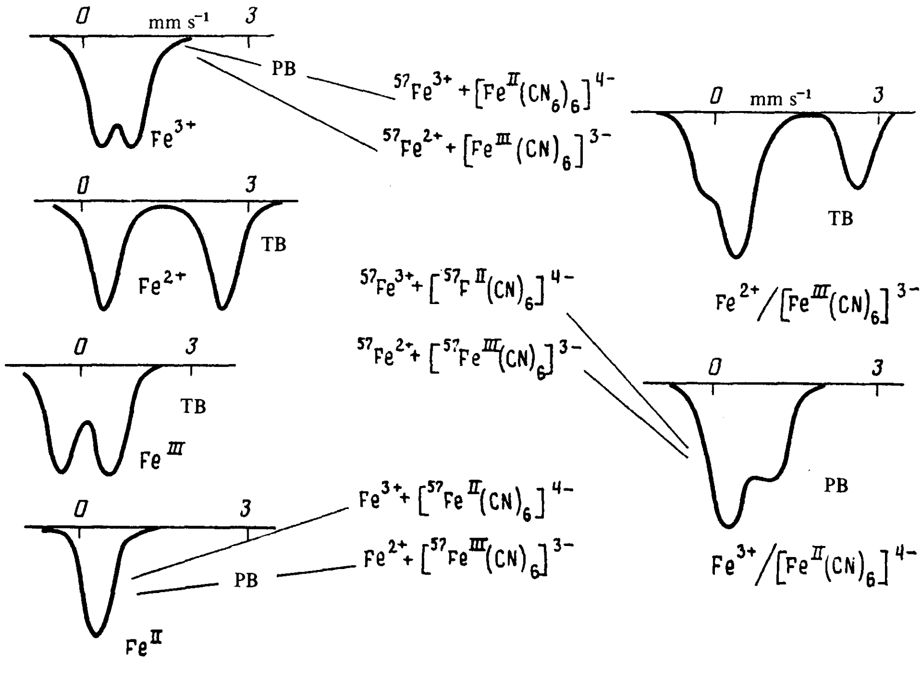

Figure 2. Mössbauer spectra of four different forms of iron.

Various chemical consequences of nuclear transformations, for example, the "shake-up" of the electronic shells as a result of the rapid change of nuclear charge and the subsequent Auger transitions, the Coulombic explosions of multiply ionised molecules, local heating, autoradiolysis, etc., are well known. Here we shall not discuss such processes (they are usually completed before the population of the 14.4 keV level of ^{57}Fe) and shall confine ourselves to chemical relaxation proper. This means, that we shall deal only with systems where the pre-Mössbauer nuclear transformation ^{57}Co → ^{57}Fe does not alone lead to an alteration of the ligand environment or the charge state of the daughter Mössbauer atoms (^{57}Fe), which are stabilised in the same environment and in the same valence state as the parent (^{57}Co) radioactive atoms. Since, however, certain chemical (valence and spin) states, which are entirely stable for the parent atom, prove to be unstable for the daughter atom (with an excited Mössbauer nucleus), the system will tend to a stable state, i.e. will undergo chemical relaxation.

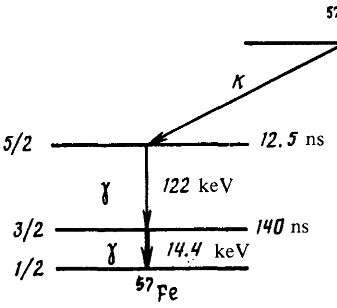

Figure 4. Schematic illustration of the radioactive decomposition (*K* capture) of ^{57}Co and subsequent γ-transitions for ^{57}Fe.

Precisely this situation has been observed[12–16] for ^{57}Co-labelled TB-like compounds of the kind of ferrous cobalticyanide $Fe^{2+}/[^{57}Co^{III}(CN)_6]$ and cobaltous ferricyanide $^{57}Co^{2+}/[Fe^{3+}(CN)_6]$. The decomposition of ^{57}Co is in this case followed by a kind of intramolecular oxidation-reduction reaction, in which the low-spin tervalent iron plays the role of the oxidant and the high-spin bivalent iron acts as the reductant. As a result, TB is rapidly converted into PB and is not therefore manifested in the usual absorption spectra, but it ultimately proved possible to demonstrate the initial formation of the short-lived TB with the aid of MES.

The search for the short-lived TB by MES methods was carried out using both the IMES and DMES (t = 0–60 ns) versions. The experiments with labelled cobalticyanide sources $M^{n+}/[^{57}Co^{III}(CN)_6]^{3-}$, where $M^{n+} = Ni^{2+}, Co^{2+}, Cu^{2+}$, and Fe^{3+} and with the $^{57}Co^{2+}/[Fe^{II}(CN)_6]$ source revealed the formation of daughter ^{57}Fe atoms in the same states as those in which the parent ^{57}Co atoms existed[17,18] and thus demonstrated the absence of appreciable chemical consequences in the emission spectra due to the effect of the *K*-capture in ^{57}Co. The cobaltous ferricyanide $^{57}Co^{2+}/[Fe^{III}.(CN)_6]^{3-}$ was used as the source, while potassium ferrocyanide $K_4Fe^{II}(CN)_6.3H_2O$ served as the absorber in the first MES experiments carried out at 77 K.[12] The results for the IMES and DMES (t = 0–60 ns) versions are presented in Fig.5.

Subsequent measurements[13] using the IMES version were performed on another source—of the type of cobaltous ferricyanide $Na^{57}Co/Fe^{III}(CN)_6$, and at lower temperatures, down to 12 K (Fig.6). It is evident that the contribution of the broad Fe^{2+} doublet (which is altogether absent from the absorption spectra owing to the instability of the TB) is in this case much greater than for IMES at 77 K. This fact reflects the retardation of the transformation TB → PB when the temperature is reduced from 77 to 12 K.

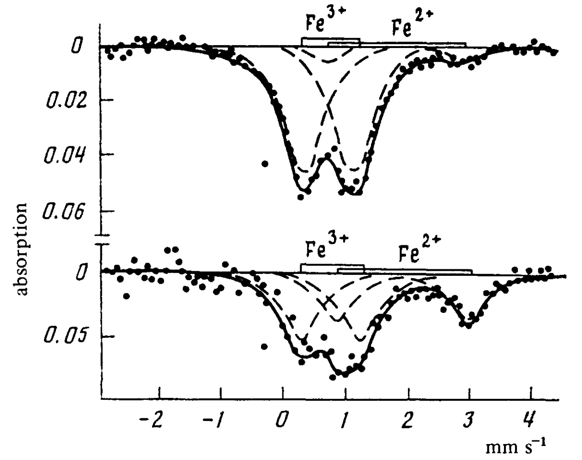

Figure 5. Mössbauer emission spectra of cobaltous ferricyanides $^{57}Co^{2+}/[Fe^{III}(CN)_6]$ at 77 K:[12] above—IMES; below—DMES (0–60 ns). The positions of the peaks of the narrow Fe^{3+} doublet and the broad Fe^{2+} doublet are indicated.

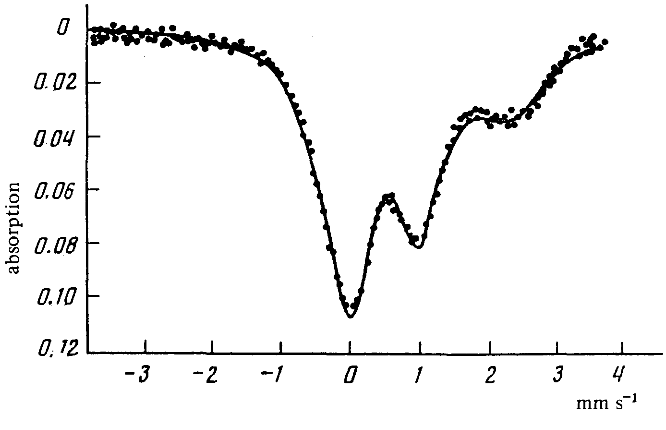

Figure 6. Mössbauer emission spectrum, integrated with respect to time (IMES), of $Na^{57}Co/[Fe^{III}(CN)_6]$ at 12 K.[13]

For an approximate (but sufficiently reliable) estimate of the rate of electron transfer in the transformation TB → PB, we shall employ a simplified representation of the observed emission spectra as a superposition of two undistorted components—the narrow Fe^{3+} (PB) and the broad Fe^{3+} (TB) symmetrical quadrupolar doublets (assuming that in this case

$f_{\mathrm{PB}} = f_{\mathrm{TB}}$). Under these conditions, the contribution of TB to the DMES spectra, obtained with a "window" of delayed $\gamma\gamma$-coincidences between $t = 0$ and $t = \tau$, should be given by

$$P_\tau = P_0\lambda\,[1 - \mathrm{e}^{-(\lambda+k)\tau}]/(\lambda + k)\,(1 - \mathrm{e}^{-\lambda\tau}),$$

where $\lambda = \tau_M^{-1}$, k the rate constant for the chemical transition (TB → PB), and P_0 the initial population of the TB state. With increase of τ, P_τ should diminish, approaching at $\tau \to \infty$ the value $P_\infty = P_0\lambda/(\lambda + k)$, characteristic of measurements by the IMES method.

The values of k obtained in this way in the range from 77 to 400 K are presented on the left-hand side of the curve in Fig. 7.[14] The right-hand side of the curve demonstrates the data obtained over the range 77–12 K with the aid of the IMES version in our joint study with the Helsinki group,[13] using the $\mathrm{Na^{57}Co/[Fe^{III}(CN)_6]}$ source. It follows from Fig. 7 that the temperature variation of the rate of electron transfer from $\mathrm{Fe^{2+}}$ to $\mathrm{[Fe^{III}(CN)_6]}$ gradually changes in accordance with a function of the Arrhenius type at temperatures above approximately 200 K (the activation energy E reaches here the value $E \cong 0.025$ eV) up to the low-temperature plateau at $T \lesssim 50$ K.

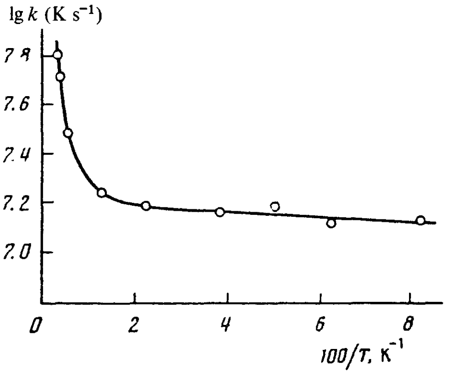

Figure 7. Temperature dependence of the rate constants for the TB → PB transition (data from Refs. 12 and 13 generalised and analysed in Ref. 14).

In this case the study of the rapid intramolecular transfer by the MES method came into contact with another field of our research—the problem of quantum (tunnel) chemical reactivity at low temperatures.

In our early theoretical studies on this problem,[19,20] the criterion of the "tunnel temperature" was introduced:

$$T_t = \frac{\hbar\sqrt{2}}{k_{\mathrm{B}}\pi d}\left(\frac{E}{m}\right)^{1/2}$$

where E is the height and d the width of the activation barrier and m is the mass of the tunnelling species. The high-temperature Arrhenius region is located above T_t, while below T_t is the region of the exponential predominance of tunnelling, which ultimately ensures the attainment of a plateau—the low-temperature quantum limit of the rate of the chemical reaction.

Within the framework of the theory of non-radiative transitions, two types of tunnelling, characteristic of different chemical reactions,[5] are considered and are usually referred to as the electronic-nuclear tunnelling and molecular tunnelling. Both these types of tunnelling lead to the appearance of a low-temperature plateau in the rate of reaction and the presence of such a plateau is regarded as proof that tunnelling predominates. The electronic-nuclear tunnelling was discovered in 1966 by Chance and de Vault in relation to the oxidation of cytochrome *c* by chlorophyll[21] and has also been observed, starting in 1971,[22] for many instances of the long-range electron transfer (over tens of angstroms) between donors and acceptors—variable valence ions.

Molecular tunnelling, observed in the form of a low-temperature plateau in the rate of the "true" chemical reaction in the full sense of these words (which rules out molecular rearrangement, steric rearrangement of atoms, and changes in valence bond lengths and angles) was discovered in 1973 in relation to the polymerisation of formaldehyde.[23]

The conversion of TB into PB was the first observed instance of intramolecular electron transfer via electronic-nuclear tunnelling. In contrast to the tunnelling of free electrons in solid-state physics, their "chemical" tunnelling is associated with the displacement of the nuclei and hence electronic-nuclear tunnelling is associated with a definite breakdown of the Franck–Condon principle.

The probability of a non-radiative electron transfer W_{if} is determined by the overlap of the electronic (ψ_e) and nuclear vibrational (ψ_v) wave functions in the initial (i) and final (f) states, described respectively by the electron transfer matrix element $L_e^2 = |\langle\psi_{e_i}|\hat{L}|\psi_{e_f}\rangle|^2$ and the Franck–Condon factor $F_V = |\langle\psi_{\nu_i}|\psi_{\nu_f}\rangle|^2$:

$$W_{if} = \frac{2\pi}{\hbar} L_e^2 F_v \rho_f,$$

where $\hat{L}$ is the transition operator of the type for non-abiabatic conditions and $\rho_f \sim (\hbar\omega)^{-1}$ the density of the vibrational levels in the final state (it is assumed that the dissipation of the heat of exothermic transitions in solids in the form of phonons occurs very rapidly and does not limit the observed rate of reaction).

The electronic-nuclear tunnelling is illustrated schematically on the left-hand side of Fig. 8. The penetration of the electron through the potential barrier (with a width l and a height E) is in this case accompanied by a much smaller barrier-free displacement (d) of nuclei. However, with increase of d whereupon the nuclear shift greatly exceeds the amplitude of the nuclear vibration Δ [for the nth vibration level of a harmonic oscillator, $\Delta_n = (2n+1)^{1/2}(\hbar/M\omega)^{1/2}$, where M is the nuclear mass and ω the characteristic vibration frequency], a potential barrier to nuclear transfer also appears (Fig. 8a) and the possibility of chemical reaction via molecular tunnelling arises. The wave functions $\psi_e(x)$ are proportional to $\exp(-x/\alpha)$ (for $x > \alpha$), where $\alpha = \hbar/(2mE_e)^{1/2}$, and for $l \gg \alpha$ the matrix element L_e^2 assumes the form of a tunnel factor of the Gamow type: $L_e^2 \sim \exp[-\beta l(m_eE_e)^{1/2}/\hbar]$, where $\beta \sim 1$ (and depends on the form of the barrier) and m_e is the mass of the electron.

This expression for L_e^2 is valid in the region of the low-temperature plateau, while above the "tunnelling temperature"

$$T_{te} = \frac{\hbar\sqrt{2}}{k_{\mathrm{B}}\pi l}\left(\frac{E_e}{m_e}\right)^{1/2} \cong 12\,000\,\frac{E_e^{1/2}}{l}$$

(Here E is expressed in eV, l in Å, and T_{te} in K) a temperature dependence of the Arrhenius type is valid:

$$L_e^2 \sim \exp(-E_e/k_{\mathrm{B}}T).$$

The wave functions $\psi_\nu(x)$ are proportional to $\exp[-(x/\Delta)^2]$ (for $x > \Delta$) and, for the Franck–Condon factor can therefore be represented by $F_\nu \sim [\exp -(\kappa d/\Delta)^2]$, where $\kappa \sim 1$. Since the statistically averaged vibration amplitude increases with temperature and for a harmonic oscillator $\langle\Delta^2\rangle$ is proportional to T for $k_{\mathrm{B}}T \gg \hbar\omega$, the behaviour of the Franck–Condon factors at high temperatures is of the Arrhenius type for both barrier-free and sub-barrier nuclear shifts.

With decrease in temperature, whereupon Δ approaches the amplitude of zero-point vibrations, Δ_0, the Franck–Condon factor reaches a minimal constant value (like also L_e^2), which leads to the appearance of a low-temperature plateau in the overall rate (W_{if}) of the non-radiative transition.

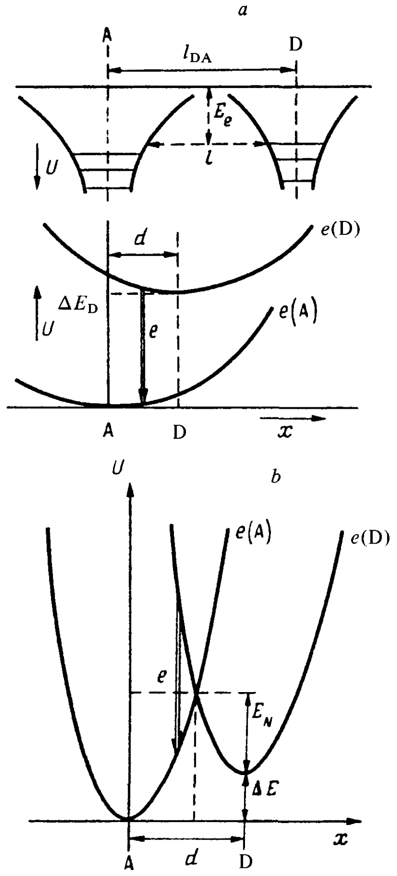

Figure 8. Schematic illustration of the electronic-nuclear tunnelling in electron transfer from a donor (D) to an acceptor (A): *a*) electron tunnelling over a distance l_{DA} through a barrier with a height E_e; such an electron transfer, symbolised below by a vertical arrow between two potential curves for internuclear interaction, corresponding to the states e(D) and e(A), is accompanied by a barrier-free shift of nuclei over a distance d; *b*) the nuclear shift d in the electron transfer from the donor to the acceptor is so great that the potential barrier with a height E_N and a width d arises between the two e(D) and e(A) potential curves (the heat of the transition is ΔE).

In the simplest case of resonance nuclear tunnelling, the Franck–Condon factor assumes the Gamow form (see, for example, Jortner and Ulstrup[24]) and the "tunnelling temperature" T_{tN} for the nuclear shift is

$$T_{tN}=\frac{\hbar}{k_B\pi\sqrt{2}d}\left(\frac{E_N}{M}\right)^{1/2}\cong 20\frac{E_N^{1/2}}{d}$$

(here E is expressed in eV, d in Å, and T_{tN} in K) for iron nuclei.

The structure of ferric ferrocyanide crystals is well known and corresponds to the interionic electron tunnelling distance $l \sim 5$ Å. The typical energy of charge transfer from the metal to the ligand in complexes of transition metals in the first row is $E_e \cong 4$ eV.[25] Consequently, the tunnelling factor of the Gamow type for a parabolic barrier ($\beta = \pi\sqrt{2}/2$) is close to 2.5×10^{-4}. The overall factor associated with the retardation of the transformation TB → PB on the low-temperature plateau, where the rate constant $k \sim 10^{-7}$ s^{-1}, amounts to $\sim 10^{-7}$, which means that the contribution of the nuclear shift (the Franck–Condon factor) to such retardation is virtually the same as for the tunnelling of the electron:

$$F_v \sim \exp[-(\varkappa d/\Delta_0)^2] \cong 4\cdot 10^{-4}.$$

The estimated value $\kappa d/\Delta_0 \sim 2.8$ can be compared with the probability of the Mössbauer effect for PB at low temperatures: $f' = \exp[-(\Delta_0/\lambda)^2] \cong 0.6$, where $\lambda = 0.14$ Å.

Thus $\Delta_0 \cong 0.1$ Å and $\kappa d \cong 0.3$ Å. Together with $E_A \cong 0.025$ eV, this reasonable estimate corresponds, in the case of a resonance nuclear shift, to $T_t \sim (10\kappa)$ K and thus confirms the conclusion that it is in fact the nuclear shift and not the electron transfer which is the process determining the appearance of the plateau in the rate of the transformation TB → PB, but only at $T \lesssim 50$ K and not at higher temperatures, where thermally activated electron tunnelling takes place.

Thus the combination of the experimental data for the rate of the chemical reaction on the low-temperature plateau ($\tau_r \cong \tau_M$), of the values of f' at $T \to 0$, and of the tunnelling temperature leads to fairly reliable estimates of both κ and d.

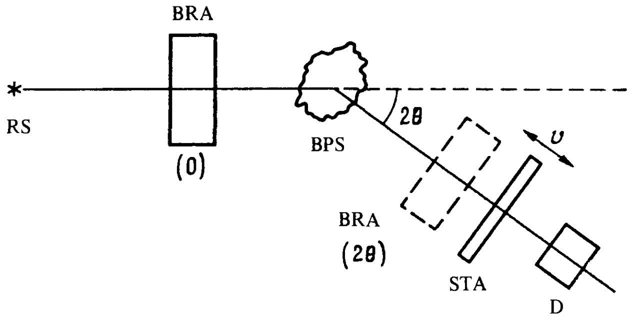

Figure 9. Schematic illustration of experimental observation of the RSME: RS—resonance source; BRA—"black" resonance absorber ensuring effective absorption throughout virtually the entire width of the Mössbauer line (it is placed either before the scatterer or beyond it—at an angle 2θ); BPS—biopolymeric scatterer; STA—standard thin absorber for the measurement of the line form by varying the rate of its movement ν; D—scintillation detector of γ-quanta, operating as the resonance detector together with the BRA.

III. STUDIES OF THE DYNAMIC PROPERTIES OF BIOPOLYMERS BY THE RSME METHOD

Extensive possibilities for the dynamic investigation of various chemical and especially biological systems have arisen as a result of another modern Mössbauer spectroscopic method—the observation of the Rayleigh scattering of the Mössbauer emission (RSME).[26–38] Leaving to one side its most informative (but also the most difficult to apply) version—coherent RSME, we shall consider only non-coherent scattering data.

The usual Mössbauer method involves the employment of a resonance source and a resonance absorber (or scatterer), while the detector is usually of the non-resonance type. The RSME method is based on the combination of the resonance source and the resonance detector for γ-rays (Fig.9). The exceptionally high energy resolution of the method (~10^{-9} eV) ensures the possibility of eliminating all non-elastic processes and a reliable determination of the contribution of elastic scattering against their background, where the elastic scattering itself is atomic and not nuclear in nature and takes place on the electron shells. In RSME observations there is therefore no need to have Mössbauer nuclei in the test specimens; Rayleigh scattering can be observed successfully and can yield valuable information for any substances in both solid and liquid phases, in the crystalline and amorphous states, and over wide ranges of temperatures, degrees of hydration, and other variables.

These features in fact determine the advantages of RSME in the study of biopolymers compared with other dynamic methods, the interpretation of the results of which also involves the use of Van Hove correlation functions, such as X-ray dynamic analysis (XDA) [39–41] and the usual MAS.[42–45]

Table 2. Biopolymers investigated by the method based on the Rayleigh scattering of the Mössbauer emission (RSME) and the information obtained.

Substance	MW	Information*	Refs.
Metmyoglobin (of the whale)	17 800	$f_R(T)$, $\Delta\Gamma_R(T)$ (T=100—300 K; h=0,05—2.3; (crystal)	[33. 46]
Trypsin	23 300	$f_R(T)$; $\Delta\Gamma_R(T)$ (T=100—300 K; h=0.1; 0.5; 0,8); $f_R(h)$ at $T\cong300$ K (h=0.1—1)	[36]
Human serum albumin (HSA)	66 500	$f_R(T)$; $\Delta\Gamma_R(T)$; $f_R(h)$ (T= =100—300 K; h=0.1—0.7); $f_R(\eta)$	[37. 38]
Chromatophores:			
Rhodospirillum Rubrum	~10^7	$f_R(T)$; $f_R(h)$	[34]
Ect. Shaposhnikovii	~10^7	$f_R(T)$; $f_R(h)$; $f_R(\eta)$	[35]
DNA (from ox spleen)	(1.5—3.0)·10^6	$f_R(T)$; $\Delta\Gamma_R(T)$; $f_R(h)$	[46]

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*The information obtained represents the functional dependence of the probability of the elastic RSME (f_R) and of the width of the RSME resonance line (Γ_R) on the temperature T, the degree of hydration h (grammes of water per gramme of biopolymer), and the viscosity of the surrounding medium η. The viscosity was varied by adding glycerol (HSA, chromatophores) and glutaraldehyde (HSA).

A general description of the RSME theory and methods is available in a number of communications (see, for example, **Refs.26–28**), while our previous studies (for example, **Refs.29–38**) were concerned with both theoretical and experimental aspects of the application of incoherent RSME to the study of the dynamic properties of biopolymers. Here we shall confine ourselves to the description of certain typical results and the most important conclusions. The biopolymers investigated and the conditions in their study (temperature, degree of hydration) are listed in Table 2.

The probability f_R of the elastic RSME served as the fundamental initial dynamic characteristic of all the objects studied. This probability is proportional to the generalised Debye–Waller factor:

$$\exp(-2W)=\exp(-Q^2\langle x^2\rangle)$$

(here $Q = 4\pi \sin\theta/\lambda$ is the momentum transferred in scattering through an angle 2θ) and thus makes it possible to determine the averaged, generalised mean-square shift $\langle x^2\rangle$, which is assumed to be the same, in such general treatment, for all the atoms of the test specimens.

Additional dynamic information can be obtained by analysing the shape of the RSME spectral lines and by comparing the observed changes in this shape (or its constancy) with the expected increase of the line width Γ_R with decrease of f_R.[29–38]

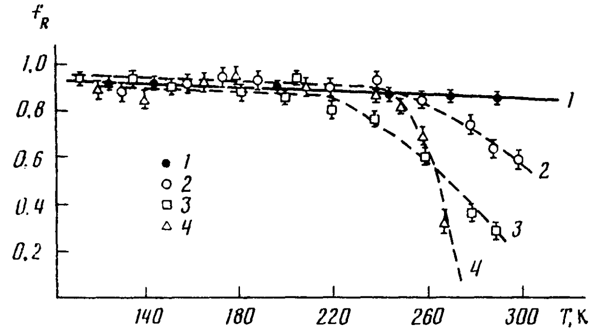

Figure 10. The contribution of elastic scattering as a function of temperature for different metmyoglobin specimens:[33] *1*) for P/P_S = 0.37 (h = 0.05); *2*) crystalline metmyoglobin; *3*) for P/P_S = 0.94 (h = 0.5); *4*) aqueous solution (26.6% metmyoglobin; h = 2.3).

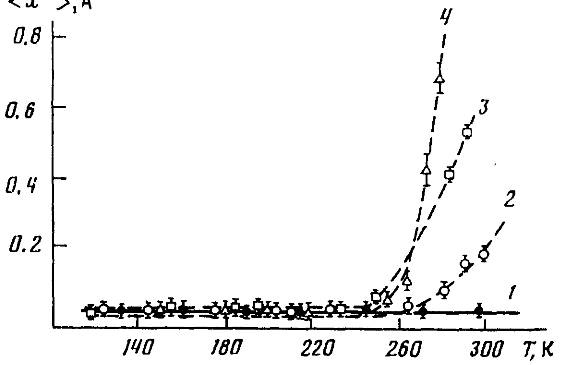

Figure 11. Generalised mean-square shift $\langle x^2\rangle$ as a function of temperature for different metmyoglobin specimens;[33] for the designation of the curves and points, see the legend to Fig.10.

A characteristic feature of the spectra of all the hydrated specimens (with a degree of hydration $h \gtrsim 0.3$ g of water per gramme of the biopolymer) was a sharp decrease of f_R at $T \gtrsim 220-230$ K, i.e. a sharp increase of the generalised mean-square shift, which reached extremely high values: $\langle x^2 \rangle \cong 1$ Å^2 for $h \cong 0.7$ and $T \cong 300$ K,[37] while the decrease of f_R at $T = 100-300$ K for dry specimens ($h \cong 0.05$) is linear and altogether insignificant: for example, $\langle x^2 \rangle \cong 0.05$ Å^2 at $T \cong 300$ K.[35]

The temperature variations of f_R and $\langle x^2 \rangle$ for metmyoglobin for different values of h [31] are presented in Figs.10 and 11. These data reveal a characteristic feature of the dynamics of biopolymers—a sharp decrease of f_r and a corresponding increase of $\langle x^2 \rangle$ in the high-temperature ($T \gtrsim 220$ K) region with increase of the degree of hydration h.

A typical example is provided by human serum albumin (HSA) at $T \cong 300$ K (Fig.12). The observed dependence of f_R on h is in this case much more pronounced than might have been expected if the mobilities of the protein as such and of the much more mobile solvent (water) had been additive. Even for high degrees of hydration ($h \cong 0.8$), the added portions of water continue to cause additional loosening of the proteins increasing the mobility of the protein globule.

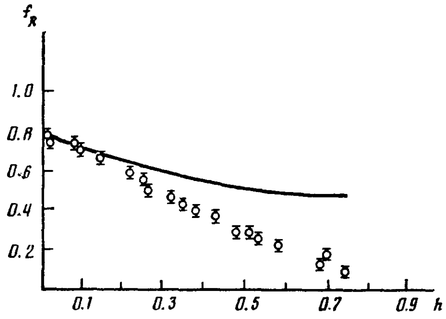

Figure 12. The contribution of elastic RSME as a function of the degree of hydration for human serum albumin at 300 K: symbols—experimental data; curve—calculation assuming simple additivity (without any correlations between the values of f_R for the protein and the solvent).[38]

The dependence of the generalised Debye–Waller factor for biopolymers on two parameters—temperature and degree of hydration—can be represented by a three-dimensional f_R (T, h) diagram, illustrated schematically in Fig.13.

The sharp decrease of the probability of the elastic RSME for biopolymers with increase of D and h is not accompanied by any serious broadening ($\Delta\Gamma$) of the spectral line. For example, the shapes of the RSME $g(\omega)$ lines for crystalline metmyoglobin at 240 and 300 K are virtually identical (Fig.14), while an almost fourfold decrease of f_R for HSA with increase of the degree of hydration (from $h = 0.05$ to $h = 0.73$) is accompanied by only a slight ($\Delta\Gamma \cong 0.10$ mm s^{-1}) broadening of the principal, "narrow" component of the RSME spectrum and by the appearance of a fairly weak broad component (Fig.15).

Such properties of the RSME spectra of biopolymers can be described by neither the Debye nor the Einstein models of the solid state nor by the picture representing a free liquid with spatially unlimited diffusion, to which the relation $f_R \cong \Gamma/(\Gamma + \Delta\Gamma)$ would have corresponded. Since the temperature dependence of the Debye–Waller factors and the line width for RSME is very similar to that for MAS (however, hydration effects have not been investigated by the MAS method), the RSME data can be interpreted by the procedures developed in recent years for the analysis of MAS results (see, for example, Refs.47–51) and based on the model representing continuous spatially limited diffusion, i.e. a Brownian harmonic oscillator with pronounced decay.

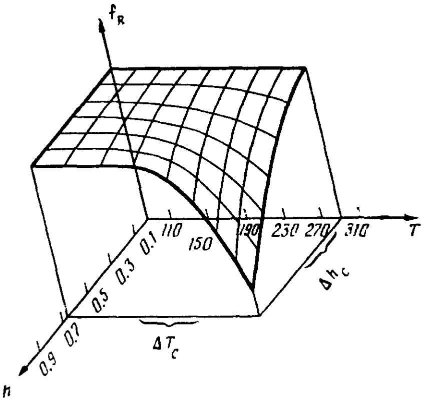

Figure 13. Three-dimensional diagram illustrating the dependence of the contribution by the elastic RSME on temperature and the degree of hydration.[46]

The physical foundations for such an approach appeared in 1973–1979 in the form of the idea of the existence of conformational substates (CSS) or, in other words, quasi-degenerate conformational states (QDCS) of protein globules, i.e. surfaces of a given macromolecule with the same overall structure which are almost degenerate in terms of energy and differ only slightly in terms of the local configurations.

Regardless of the approach to the treatment of QDCS [as "mobile defects",[52] treatment aided by the computer modelling of the dynamic properties of proteins[53] on the basis of the polychromatic kinetics of the Fe–CO recombination in haem-containing proteins,[54,55] or X-ray-dynamic analysis (XDA) [39–41]], the QDCS concept implies a definite modification of the understanding of protein structure (the structure of biopolymers in general) in the spirit of the scheme illustrated in Fig.16. Until the appearance of the QDCS concept, it was usually assumed that, in conformity with the familiar Schrödinger[56] definition of a protein as an aperiodic crystal, each individual biomacromolecule in its ground state is located in a global energy minimum and is characterised by a definite clearly fixed geometry. Within the framework of the QDCS concept, the global energy minimum for biomacromolecules is not realised at all, even as $T \to 0$, and the actual observed state is a spatially delocalised system with numerous local energy minima. The increase of the mobility of biopolymers with increase in temperature and in the degree of hydration can be described by the theoretical methods developed previously[47–51] by virtue of the stimulation of transitions between the QDCS.

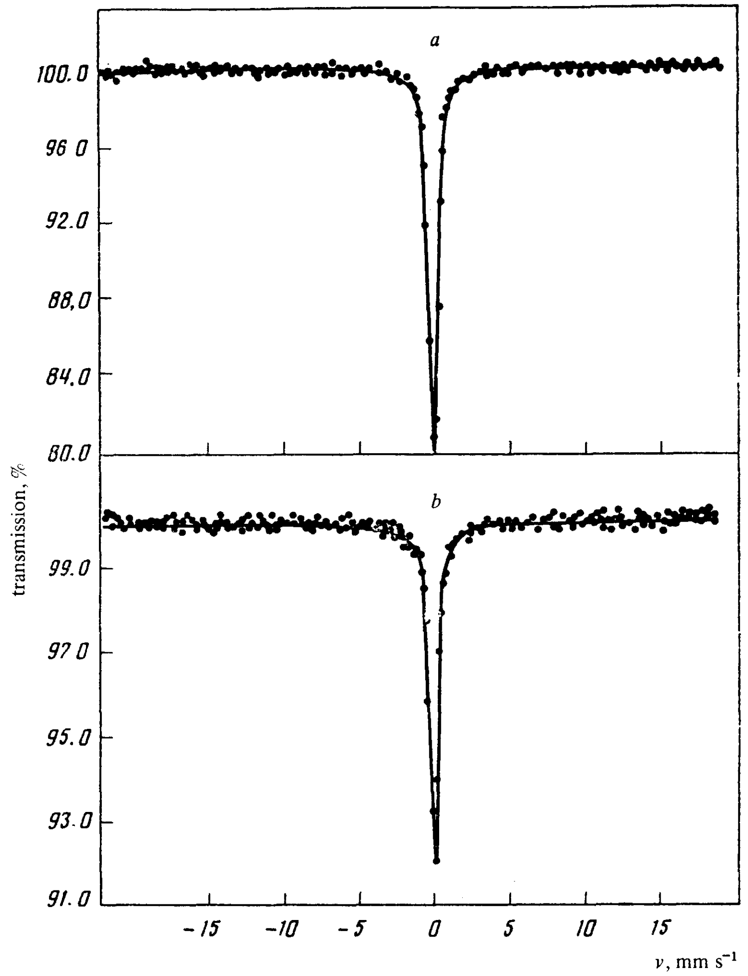

Figure 14. The RSME energy spectra for crystalline metmyoglobin at 240 K (*a*) and 300 K (*b*).[46]

The expansion of the variety of experimental MAS and RSME data necessitates further development of spatially limited diffusion models, namely a transition from the case of a single oscillator to a multimodal approximation, which presupposes the presence of at least two or three Brownian oscillators with pronounced decay. The conformational mobility of biopolymers at room temperature, determined by the MAS and RSME methods, is characterised by a fairly broad spectrum of correlation times τ_c—from 10^{-6} s (broadening of the principal, narrow, spectral line) to 10^{-9} s (contribution to the broad component) and further to even lower values of τ_c (decrease of the contribution of elastic scattering). According to data obtained by other methods (for example, the luminescence and spin label methods[57]), the range of correlation times embraces also much slower movements—down to $\tau_c \sim 1$ s. The hierarchy of the amplitudes and relaxation times of various internal motions in biopolymers is also manifested in the computer modelling of protein dynamics.[58]

A broad spectrum of relaxation times of motions is typical for the vitreous state—in contrast to the liquid and crystalline states.[59] That it is natural to compare the dynamic properties of biopolymers and glasses follows from the entire set of data for the dependence of the RSME spectra on temperature and the degree of hydration. The sharp increase of $\langle x^2 \rangle$ at the glass point T_g, similar to that observed for proteins above $T_c \cong 220$ K and also sometimes accompanied by a slight broadening of the spectral lines (when $f_R \lesssim 0.5$ to 0.1), is typical for supercooled organic liquids.[27,28] Our observations also demonstrated a clear correlation between the onset of the sharp decrease of f_R and the jump in the specific heat following an increase in temperature (DNA : $h \cong 0.6$; $T \cong 200$ K) and in the degree of hydration (lysozyme : $T \cong 300$ K; $h \cong 0.2$–0.3).[33,46] Such jumps in specific heat usually indicate the occurrence of glass points for polymers—they are absent only for a very high ($\gtrsim 75\%$) degree of crystallinity of the polymers. Additional experimental data, supporting the analogy between the dynamic properties of biopolymers and glasses, are presented and discussed in the present author's more detailed publications.[33,46]

Turning now to the three-dimensional diagram in Fig.13, it is natural to suppose that, below some kind of "critical" point (more correctly some kind of extended "critical" regions) in temperature and degree of hydration, the ground state of the biopolymer is more likely to resemble a heterogeneous glass than a crystal. As regards structural characteristics, this approach to biopolymers is consistent with Fig.16*b*—a system of local energy minima, which implies the absence of structural unambiguity in the biomacromolecule represented by a set of QDCS.

As regards the dynamic characteristics of biopolymers, we employed their heat capacity at very low temperatures as a test of dynamic vitreous properties.[46,64,65] The temperature dependence of the heat capacities of inorganic and organic dielectric glasses at low temperatures is given by

$$C_v(T) = C_1T + C_3T^3 + C_E\left(\frac{\theta_E}{T}\right)^2 \cdot \exp\left(\frac{\theta_E}{T}\right) \cdot \left[\exp\left(\frac{\theta_E}{T}\right) - 1\right]^{-2},$$

i.e., apart from the Debye (second) and Einstein (third) terms, it contains a linear term, which predominates as $T \to 0$.[60]

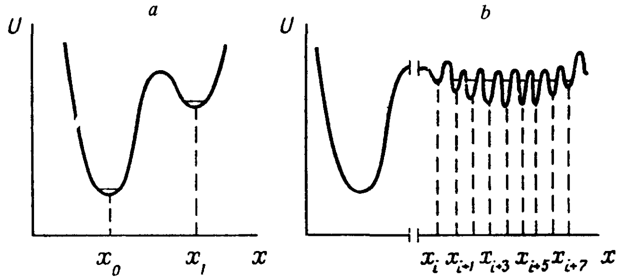

Figure 16. Potential energy curves for biomacromolecules: *a*) global energy minimum corresponds to the ground state (whose structure is unambiguously fixed as $T \to 0$), while the other minima (only one of these is shown) correspond to short-lived and weakly populated excited states; *b*) there is no global minimum at all and the system of local minima represents the spatially delocalised and energetically similar conformational substates (CSS) or quasi-degenerate conformational states (QDCS) whose populations are not unambiguously defined even as $T \to 0$.[46]

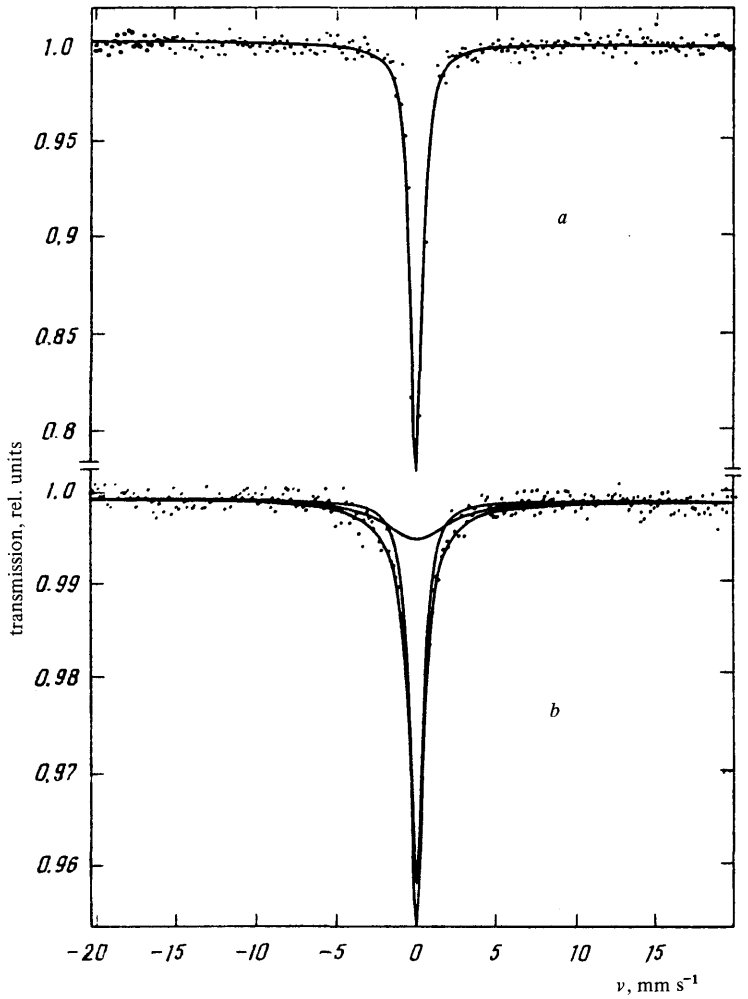

Figure 15. The energy spectra for HSA (300 K) at $h = 0.05$ (*a*) and $h = 0.73$ (*b*). For HAS with $h = 0.73$ (*b*), the overall spectrum represents a superposition of the "narrow" component (with the same line width as for $h = 0.05$) and the "broad" component, which are also illustrated in part *b* of the figure.[37]

This especially important linear contribution to the low-temperature heat capacity is associated with a fundamental property of the vitreous state—its non-equilibrium nature, the existence of a residual entropy as $T \to 0$. Its presence, magnitude, and physical significance have been explained[61,62] on the basis of the model of phonon-stimulated tunnelling (PST) in the so-called two-level (multilevel) systems, i.e. the tunnelling of atoms and atomic groups between two (or many) quasi-equilibrium positions (QEP), between two (or many) similar but non-equivalent potential wells by virtue of the adjustment of the transitional resonance between such QEP via the excitation (absorption or emission) of phonons (Fig.17).

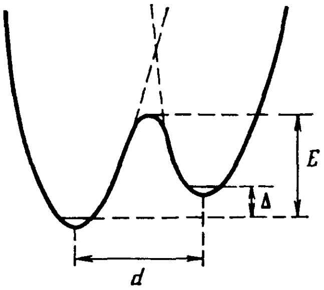

Figure 17. The simplest picture comprising two quasi-equilibrium positions (QEP) for atoms or atomic groups of biopolymer molecules (two-level system with two wells). Typical values: $E \cong 0.2$–0.4 eV, $d \cong 0.2$–0.4 Å. The resonance adjustment within the limits of the width of the energy gap Δ is ensured by phonons (phonon-stimulated tunnelling).[46]

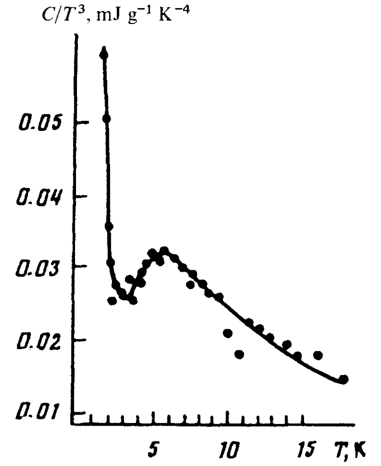

Figure 18. Experimental data[61] for the low-temperature heat capacity of HSA in terms of the function $C/T^3 = f(T)$, illustrating the presence of a linear term due to the phonon-stimulated tunnelling.

The dependence of the quantity C_1 on the spectral density of two-level states $n(\Delta)$ at $\Delta \to 0$ has the following form:[60]

$$C_1 = \frac{\pi^2}{6} k_B^2 n(0).$$

The local energy minima, illustrated in Fig.16*b* and characterising the QDCS of biomacromolecules, form precisely such a multilevel, multiwell system and it is natural to expect the occurrence of PST between QDCS playing the role of QEP.

We have analysed extensive experimental data for the low-temperature heat capacities of biopolymers (see the relevant review[63]) on the basis of the above three-term formula and observed[33,64,65] that the linear term C_1T for biomacromolecules is significant.

The results of our calculations and also of later direct experiments with HSA [66] (Fig.18) and metmyoglobin [67] are compiled in Table 3.

Table 3. Parameters of the low-temperature heat capacities of polymers and biopolymers.

Substance	C_1, μJ g^{-1} K^{-2}	C_3, μJ g^{-1} K^{-4}	$10^{-40}n(0)$, J^{-1} g^{-1}	Number of two-well systems (for Δ = 100 K)	Temperature range of measurements ΔT, K	Refs.
SiO_2	1.2	1.8	0.38	—	0.1—1.5	[60]
Poly(methyl methacrylate)	4.8	28	1.5	—	1.5—10	[60]
Melanine (1% H_2O)	5.0	12	1.6	—	2—4.5	[68]
Melanine (20% DCA)	9.5	9.9	3	—	2—4.5	[68]
Melanosoma	22	9.9	7	—	2—4.5	[68]
Poly-L-alanine (α-form)	45	25	14	—	1.5—10	[69]
Poly-L-alanine (β-form)	36	20	11	—	1.5—10	[69]
Polyglycine-P	18	8.8	59	—	1.5—22	[70]
Collagen	~10³	10	300	2.5·10³	5—20	[63]
DNA	~10		3.2	2.1·10³	0.5—5	[71]
HSA	39	8	12.5	19	1.5—25	[66]
Metmyoglobin	—	—	3.3	1.4	0.1—3	[67]

The vitreous dynamic model of biopolymers proposed by the present author and his co-workers[33,64,65] presupposes the existence of internal mobility of the biomacromolecules even as $T \to 0$ by virtue of the PST of atoms and atomic groups.

Thus we have demonstrated yet again that the modern Mössbauer spectroscopic methods constitute an effective instrument in the study of tunnelling phenomena in chemical and biochemical physics—the quantum effects in the kinetics of chemical reactions and biomolecular dynamics, which are most pronounced at low temperatures.

The RSME data can yield fairly reliable estimates of the tunnelling parameters.[33,46] The maximum values of $\langle x^2 \rangle$ at 300 K reach almost 1 Å^2 and the contribution by elastic RSME is in this case smaller by a factor $N = 4$–5 than at low temperatures. According to Shaitan,[72] the factor N means simply the number of potential wells in the multiwell region of the delocalisation of certain atomic groups. The distance between the wells is then given by $d \cong \sqrt{\langle x^2 \rangle}/(N-1) \cong 0.25$ to 0.33 Å; subsequent analysis of the temperature dependence of the parameters of three-dimensional diffusion[47-51] yields the height of the energy barrier between the wells: $E \cong 0.2$ eV and the tunnelling temperature[19,20] for CH_2 groups is accordingly estimated at $T_t \cong 120$–160 K. Inspection of the multimodal Franck–Condon effects, i.e. allowance for the low-frequency vibrations of potential wells relative to one another[73-75] (apart from the high-frequency vibrations of the tunnelling groups within the limits of the occupied wells) leads to the conclusion that, even at the physiological temperatures, the contribution of tunnelling may be quite comparable to that of thermally activated transitions of atomic groups between QEP and that tunnelling induced by fluctuations can have a definite importance also for the functioning of proteins and other biopolymers.[33,46]

Thus RSME studies on biopolymers combined with MAS and XDA data as well as low-temperature heat capacities provide an adequate basis for treating natural biopolymers as special heterogeneous glasses incorporating regions with different glass points.[33,46,64,65]

At room temperature, a biomacromolecule contains regions whose properties resemble those of a crystal, a glass, a supercooled liquid, and an ordinary liquid. The principal physical parameter, chosen here for the purpose of the description and comparison of different states, is the free volume.

The $f_R(T, h)$ three dimensional diagram (Fig.13) demonstrates the existence of a transitional ΔT_c region in the vicinity of $T_c \cong 200-220$ K and a Δh_c region in the vicinity of $h_c \cong 0.1-0.3$. For $T < T_c$ and $h < h_c$, the dynamic properties of biopolymers combine the properties of a crystal and a glass, while above T_c and h_c they combine the properties of a crystal, a glass, and a supercooled liquid.

The temperature T_c plays the role of the usual glass point T_g and the degree of hydration h_c plays the role of a kind of hydration glass point h_g for those regions in biomacromolecules where the glass state is transformed into the highly elastic state. The increase of the specific volume (and also of the free volume) of the biopolymer and hence of its internal mobility with increase of temperature and of the degree of hydration accelerates appreciably at temperatures above T_c and for $h > h_c$.

All the above considerations are summarised in Table 4, where the plus and minus signs denote the presence or absence of the following four main properties: (a) order; (b) periodicity of the structure (for an individual biomacromolecule); (c) unambiguity of the structure (for an individual biomacromolecule) as $T \to 0$; here the plus sign denotes that $S_0 = 0$ at $T = 0$ and the minus sign denotes that $S_0 \neq 0$; (d) mobility as $T \to 0$.

Table **4**. Description of the parameters of the structural and dynamic properties of biopolymers.

Substance	Order	Periodicity	Unambiguity of structure*	Mobility*	Glass:IC number***
Ideal crystal	+	+	+	−	
Glass	−	−	−	+**	
Aperiodic crystal	+	−	+	−	1:3
Biopolymer (treatment after 1973-1979)	+	−	−	−	2:2
Biopolymer (treatment after 1983)	+	−	−	+	3:1

*As $T \to 0$.

**Treatment after 1972.

***Here IC = ideal crystal.

The ideal crystal (+++−) and glass (−−−+) (the plus sign denoting mobility in glasses has been generally accepted since 1972 [61,62]) are used in Table 4 as the principal comparison standards. The Schrödinger definition[46] of the protein as an aperiodic crystal is designated by the symbol (+−+−), the appearance of the concept of CSS (QDCS) (1973–1979) [39−41, 52−55] denotes the transition to (+−−−), and finally the vitreous dynamic model of proteins (1983) [33,64,65] corresponds to the formulation (+−−+). Thus the general ratio 3:1 in favour of the ideal crystal has gradually changed to 1:3 in favour of glass.

* * *

We have thus seen that gamma-resonance spectroscopy in its MAS and RSME versions has played a very notable role in the development of ideas about the structural and dynamic properties of biopolymers, i.e. in one of the most important problems of modern biochemical physics.

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Chemical, Physical, and Biological Approaches to the Creation of Stabilised Enzyme Catalysts for Biotechnology

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The problem of the inter-relation between the structure and stability of proteins includes two main questions: firstly, how can we discover the molecular characteristics of the structure of proteins which are responsible for their stability? Secondly, how, knowing the general molecular causes of stability, can we alter the structure of a specific protein in order to increase its stability, i.e. to stabilise it? In the present review an attempt is made to present the current state of both the first (fundamental) and second (applied) aspects of this problem.
The bibliography includes 250 references.

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I. INTRODUCTION

The problem of the inter-relation between the structure and stability of proteins is one of the key problems in modern protein chemistry.[1] Only its solution will permit a close approach to the realisation of the long-standing aim of investigators in the field of protein chemistry: to predict[1,2] the steric structure of the protein from its known aminoacid sequence and to attempt the synthesis[3] of a molecule of a protein type whose property is specified beforehand.

On the other hand, one of the central tasks of chemical (engineering) enzymology is to create stabilised enzyme preparations for various technological applications.[4-11] The pathway leading to the creation of stabilised enzymes was outlined several decades ago when many world laboratories began to elucidate and investigate the molecular mechanisms or at least the molecular causes of the inactivation of protein (see the relevant reviews[12,13]). Only after this "preparatory stage" did it become possible to proceed directly to the development of methods whereby the structure of enzymes could be influenced specifically in order to suppress the inactivation mechanisms established previously. The chemical and physical methods for the stabilisation of enzymes have so far been developed to the greatest extent (see the relevant reviews[14-19]). However, there is no doubt that the biological approach proposed recently (application of methods of genetic engineering)[20-22] merits no less attention.

The present review deals with the entire chemical-physico-biological set of inter-related problems. The data described have been divided into three somewhat separate sections. Firstly, there is a brief discussion of experimental and theoretical approaches used to establish the inter-relation between the stability of proteins and their structure. This is followed by the molecular causes of the stability of proteins themselves. This question has been frequently raised in the literature at least since the studies by Bressler and Talmud.[23] The current level of the problem has been fairly completely dealt with in recent publications, for example, in the monograph of Schultz and Schirmer.[1] We should therefore attempt here mainly to answer the following question: what must be done to the protein (how must its structure be altered) in order to impart to it greater stability. Finally, in the last Section it is shown how this can be achieved at the present time, i.e. the experimental methods for the preparation of highly stable biocatalysts are examined.

II. THEORETICAL AND EXPERIMENTAL APPROACHES TO THE ELUCIDATION OF THE INTER-RELATION BETWEEN THE STRUCTURE AND STABILITY OF PROTEINS

The solution of the problem of the inter-relation between the structure and stability of proteins in the most general form implies the calculation of the free energy of the protein from its steric structure. In principle, one could attempt to calculate separately for this purpose the energy of each of the stabilising (hydrogen bonding, hydrophobic, electrostatic, and dispersion interactions, etc.) and destabilising (in the first place the unfavourable entropy contribution by a strained conformation) factors and to add them up. Unfortunately, this cannot be carried out correctly.[1,24] The reason is that the contribution of each of the above components to the free energy of the protein amounts to tens and hundreds of kcal mol^{-1}.[25,26] This is a lot in view of the fact that proteins as a whole are characterised by a relatively low stability; the experimental free energy of stabilisation (of the native form relative to the denatured form) amounts to between 5 and 15 kcal mol^{-1} for the vast majority of globular proteins.[27]

Another general (experimental) way of solving the problem consists in the following procedure: one selects two proteins of different stability and by comparing their structures one attempts to elucidate how the structural characteristics are responsible for the increased stability of one of them. However, the following question arises: which pair of proteins should be chosen for such a comparison? If we select two arbitrary proteins, then in all probability their stabilities will be found to lie in the statistical average range of free energies: 5–15 kcal mol^{-1}. Consequently the differences in stability will be minute and it will be hardly possible to identify them with any definite structural characteristics, especially against the background of the large structural differences characteristic of functionally different proteins.

The same feature of protein structure (small differences in stability against the background of a great structural variety) lead apparently to a relatively low predictive value of studies of a generalised character.[28-31] In other words, the attempts to analyse the known structure of several tens of proteins in order to find a correlation between their stability and certain general structural parameters (hydrophobic nature,[28-30] volume,[30] or the content of particular aminoacid residues[31]) did not lead to unambiguous conclusions.

Comparison of the stabilities of proteins having fairly close structures proved to be most fruitful. Proteins having the same biological function are characterised by such structural kinship.

A typical experiment designed to elucidate the inter-relation between structure and stability consists of three stages. Firstly, two (or several) functionally related proteins from different sources are selected and are obtained in as pure a form as possible. Next, the following characteristics of the proteins are compared: (1) the aminoacid compositions and primary structures; (2) the steric three-dimensional structures and parameters of their conformational variability; (3) the resistance to the action of reversible denaturing agents and to irreversible investigation; (4) the temperathre dependence of the functional (catalytic) activity.

Finally, an attempt is made to correlate the quantitative stability characteristics obtained (such as the temperature of reversible denaturation, the optimum temperature of enzyme activity, and the equilibrium or kinetic denaturation parameters—ΔG, ΔH, ΔS, etc.) with the structural differences which it has been possible to discover.

The question arises of the origin of functionally related proteins having different stabilities. In the first place, they are found in nature. Firstly, these are related proteins from different mesophilic sources. Secondly, related proteins from thermophilic and mesophilic organisms are compared. Thirdly, proteins from wild strains are compared with proteins altered by mutation. The objects of such research are also obtained artificially. Three methods are used at present for this purpose: "site-directed" mutagenesis, immobilisation, and chemical modification. We shall consider what information can be obtained from the study of the inter-relation between the structure and stability of proteins by the application of each of these approaches.

1. Homologous Proteins of Mesophilic Organisms

Comparison of the structures of enzymes fulfilling identical functions in evolutionary remote organisms has long been used to elucidate the mechanisms of enzyme catalysis.[32] However, this approach is used much more rarely for the study of the inter-relation between the structure and stability of proteins. The point is that the differences between the primary structures of related mesophilic proteins can be extremely large. For example, in two of the most widely different proteins of the family of globins, only 16% of all the aminoacid residues occupy identical positions in the primary structures.[33] On the other hand, the differences between the stabilities of homologous proteins are as a rule very insignificant—not more than 1–3 kcal mol^{-1}. The insuperable problem discussed above therefore arises: how can one interpret the minute changes in stability against the background of large differences in structure?

Nevertheless, comparison of homologous proteins of mesophilic organisms yields some useful information about the inter-relation of their structures and stabilities.[33-36] Firstly, it is sometimes possible to find related proteins which differ only by 1–2 aminoacid residues, which naturally facilitates the problem of the elucidation of their role in the stability of the proteins being compared.[19] Secondly, it is frequently possible to discover "invariant positions" in proteins (the replacement of aminoacid residues in these positions is inadmissible, because it leads to the decomposition of the structure). As a rule, the invariant positions are located either in the inner regions of the globule[33-36] or in the regions corresponding to intersubunit contacts[36] and contacts between neighbouring α-helices.[33] The aminoacid involved in the coordination of haem[34] as well as the fragments of the active centres of the enzyme[36] are also invariant.

2. Comparison of Proteins from Thermophilic and Mesophilic Organisms

The existence of life under extreme conditions has long been known—for the history of the development of the problem, see Brock.[37] It was not until the middle 1960's that it became possible to demonstrate that the stability of microorganisms under extreme conditions is as a rule associated with the increased stability of their constituent biomacromolecules and in the first place proteins.[38]

The search for differences between the structures of related thermophilic and mesophilic proteins has the advantage over the comparison of mesophilic objects that the range of the differences between their stabilities is much wider and hence there is a greater probability of observing the structural differences which are significant for stability. Hitherto ~100 thermophilic proteins have been isolated in a highly pure form and their properties have been investigated. The molecular causes of the increased stability of thermophilic proteins have been discussed in a series of reviews and monographs.[19,37-49]

3. Proteins Modified by Mutation and Proteins from Wild Strains

Under the influence of unfavourable external influences, chemical agents, irradiation, and certain other factors in nature, the phenomenon of the so called mutagenesis takes place.[50] At the level of cells and whole organisms, mutagenesis is expressed by a change in morphology and functions and frequently leads to degeneracy. At the molecular level, nucleotides are replaced, new bases (or even whole sections of the genome) are incorporated or omitted. This results in the synthesis of proteins with a modified structure: with replacement of one (the most frequent case) or several aminoacid residues by different ones; with the polypeptide chain divided into a series of fragments not linked by covalent bonds or, conversely, with covalently cross-linked polypeptide chains.[50]

Comparison of the structures of mutant proteins and proteins from wild strains is actively employed for the elucidation of the mechanisms of enzyme catalysis,[51,52] in particular in order to discover the aminoacid residues significant for catalysis.[53] Using this approach, it has been possible to obtain also information about the role of individual aminoacids and of more complex structural factors in the stability of proteins some examples may be found in the review of Mozhaev and Martinek.[19]

4. Artificially Modified Proteins

There exist at least three ways of obtaining artificially modified proteins: site-directed mutagenesis (using the procedures of genetic engineering), immobilisation, and chemical modification.

(a) The Method of Site-Directed Mutagenesis

In this method manipulation at the level of genes yields analogues of proteins with a known tertiary structure differing by the replacement of only one aminoacid residue in a rigorously specified position.[54]† The latest advances in site-directed mutagenesis[20,55] have made the method available in many laboratories. Thus proteins of "aritificial origin" modified by mutation have come to be used for the study of the role of definite aminoacid residues in catalysis.[56] Enzymes with an improved activity and an altered substrate specificity have been obtained in this way.[57,58] As for mutants of natural origin, proteins with substituted aminoacid residues in specific positions, obtained artificially (by genetic engineering), can yield information about the role of individual structural elements also in the stability of proteins.

(b) Immobilisation of Enzymes

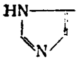
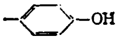
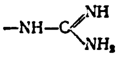
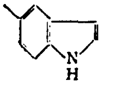
This should be understood in the first place as a method for the significant restriction of the mobility of protein molecules (or their fragments) in space or relative to one another.[59,61] In recent years this method has been used actively in biotechnology,[4–11] in particular for the stabilisation of enzymes.[14–19] However, sometimes one encounters the view that the immobilisation method is effective only for the solution of purely applied problems but does not yield new information for fundamental science. This view is based on the long-standing preconceived notion that immobilisation alters the structure of the enzyme compared with its native structure. However, it has been demonstrated in recent years by physical methods that this is by no means the case: in many instances immobilisation does not change the conformation of the enzyme at all or changes it only insignificantly (see the review of Martinek and Mozhaev[62]). Furthermore, having selected a suitable immobilisation method, one can be certain that the conformations of the native and immobilised enzymes are similar.[62] For this reason, immobilised enzymes have proved to be successful models in the study of a whole series of *in vivo* processes.[62,63] They also yield useful information about the inter-relation of the structure and stability of proteins. Thus the important role of fluctuations in the structure of the protein in its stability has been discovered with the aid of immobilisation.

(c) Chemical Modification of Proteins

This method is used as an approach not only to the stabilisation of enzymes[64–66] but also to the elucidation of the inter-relation between the structure and stability of proteins.[19,66]

The main problem involved in the use of the modification approach is that of obtaining a protein preparation in which only a specific functional group (or a specific series of groups) has been modified. The difficulty of specific modification lies in the fact that the functional groups of proteins exhibit the same type of reactivity: they are all potential nucleophiles and proton donors or acceptors (Table 1). For this reason, the "frontal" modification of proteins by an arbitrary reagent leads to competition between different functional groups of the protein for the reagent and usually ends in failure—non-specific modification. Nevertheless, advances in selective modification have led to the discovery of several reagents for virtually any functional group in proteins which involve only this particular group (for examples, see Table 1). Furthermore, even for reagents exhibiting group specificity, it is frequently possible to select conditions under which aminoacid residues of only one type are modified selectively. For this purpose, one varies either the pH (because as a rule only one of the forms—protonated or deprotonated—is reactive) or one employs reversible modification reactions (Table 2) with the aid of which other groups of the protein competing for the reagent can be subjected to preliminary blocking.

Table 1. The functional groups in proteins which can be subjected to specific modification.[72]

Group	Aminoacid residue	pK_a	Examples of selective reagents*
α-COOH	terminal aminoacid	<1—6.8	carbodiimide + nucleophile
β-COOH	Asp	<1—6.8	ditto
γ-COOH	Glu	<1—6.8	»
	His	6.4—7.5	diethyl pyrocarbonate
—SH	Cys	8.0—9.5	*N*-ethylmaleimide; disulphides
α-NH$_2$	terminal aminoacid	7.3—>12	dansyl chloride; methyl acetimidate
ε-NH$_2$	Lys	7.3—>12	ditto
	Tyr	9.4—>12	tetranitromethane, *N*-acetylimidazole
 $-NH-C(=NH)NH_2$	Arg	11.5—>12	butane-2,3-dione, phenylglyoxal
—OH	Ser, Thr	>12	—
	Trp	>12	*N*-bromosuccinimide
—S—CH$_3$	Met	—	chloramine T; H_2O_2

*Taken from Lundblad and Noyes.[89]

The potential value of the chemical modification method is truly enormous.[67–89] However, its application to the study of the inter-relation between the structure and stability of proteins encounters a series of methodological difficulties, which are frequently fundamental. We shall consider the most important of these difficulties and shall attempt to outline ways whereby they can be overcome.

1. There is a risk that modification will involve the invariant elements of the protein structure and will lead to undesirable conformational changes, up to the denaturation of the protein.[72,84] In order to test this possibility, the chemical modification product must be analysed by a physical method and it must be discovered whether the conformations of the native and modified proteins are different. If such differences exist, it is essential to alter the modifying agent.

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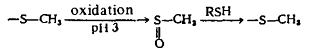
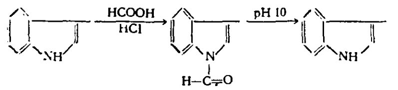
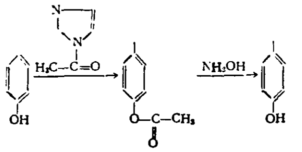
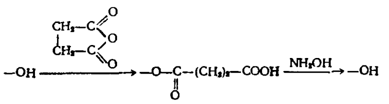
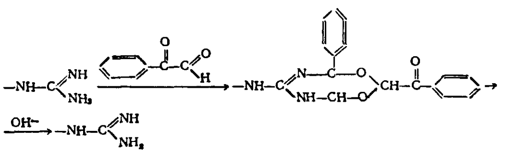
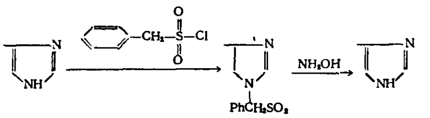
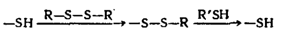
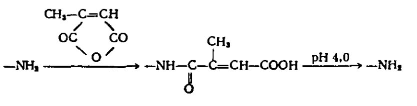
†The methodological procedures of site-directed mutagenesis will be examined below.

2. Sometimes it is necessary to modify proteins under fairly severe conditions where undesirable side processes can take place (Table 3). In order to avoid secondary reactions, it is frequently necessary to resort to preliminary protection of the "vulnerable" functional groups (Table 2) and, after the modifications have been carried out, the "protecting groups" must be removed under mild conditions.

Table 2. Reactions leading to the reversible protection of the aminoacid residues in proteins.

Amino-acid	Reaction	Refs.
Met		[90]
Trp		[91]
Tyr		[92]
Ser, Thr		[93]
Arg		[94]
His		[95]
Cys		[96]
Lys		[97]

3. Only in rare cases is it possible to modify the protein in such a way that only a specific aminoacid residue in it is involved. Usually chemical modification results in a set of derivatives of the protein differing both in the number of modified groups and in the ordinal numbers of the residues affected by the modification in the primary structure. This naturally leads to a significant inhomogeneity of the products of the chemical modification of the proteins.[72,84] The difficulty of separating the product is inherent in the fact that the modified proteins frequently differ little in their physical properties (charge, molecular weight, molecular shape, etc.). High performance liquid chromatography proved to be especially useful in this field.[98]

4. Yet another serious problem is how to identify the product of the chemical modification of the protein. Aminoacid analysis is most often used for this purpose. However, the method suffers from the disadvantage that, before the direct determination of the aminoacid composition, the protein is subjected to a treatment under extremely severe conditions (concentrated HCl, temperature above 100 °C) in order to hydrolyse all the peptide bonds. This is naturally accompanied also by the rupture of other chemical bonds (weaker than the peptide bonds) and certain aminoacids undergo chemical decomposition. For this reason, the identification of many aminoacids (Cys, Trp, Met) and of the products of certain types of chemical modification (oxidation, acylation) is either altogether impossible by means of aminoacid analysis or inaccurate results are obtained.[85,86] Fortunately, this difficulty can be overcome[85] by employing certain methodological devices (for example, reactions competing for functional groups or the radioactive tracer method).

Table 3. Undesirable side reactions in the modification of the functional groups of proteins.[84]

Functional group	Conditions	Result
Peptide bond	pH 8—12	hydrolysis
ditto	pH 1—5	N-O acyl shift
SH group	oxidation	S-S bond, S-O acids
S-S bond	reduction	SH groups, new S-S bonds
ditto	pH 8—12	hydrolysis, β-elimination
S-CH_3 group of methionine	oxidation	hydroxy-derivative
Amide group	pH 8—12	hydrolysis
O-Glycosyl group	pH 8—12	β-elimination
O-Phosphate group	pH 8—12	β-elimination

Another way of overcoming this difficulty involves the determination of the degree of modification under mild conditions. This is effectively assisted by the reactions involved in the spectrophotometric titration of the residual unmodified functional groups of the proteins with the aid of chromophoric reagents (certain examples are presented in Table 4). The methods for the determination of the primary structure are used to determine the exact site where the modified aminoacid residue is located.[103]

Thus the difficulties arising can be overcome in principle and one can proceed to the search for the inter-relation between the stability and structure of the protein. The experiment must be begun with a comparison of the conformations of the native and modified proteins. The point is that sometimes the increase[104,105] or decrease[106,107] of the stability of proteins as a result of chemical modification is caused precisely by conformational changes. Such data are of limited value, because it is difficult to interpret them and even more difficult to predict them.

One usually has to deal with a chemical modification product which, while conformationally not different from the native protein, nevertheless has a lower or higher stability. In order to elucidate the molecular causes of stabilisation or destabilisation, the following methodological procedures are employed.

The increase of the degree of modification (of the number of modified functional groups). If the stabilising or destabilising effect changes monotonically (smoothly) under these conditions, the most likely implication is that specific interactions of any kind, for example, the formation of salt bridges or hydrogen bonds, do not arise (or vanish) in the protein on modification. Otherwise, the observed dependence would have been of a discrete type: indeed, it is difficult to imagine that the modification of each successive residue generates or destroys a salt bridge or hydrogen bond. It is more probable that the smooth type of dependence of the stabilising or destabilising effect on the degree of modification reflects a uniform alteration of some integral parameter of the globule (its hydrophobic property or surface charge).

A change in the chain length of the modifying agent for a specified degree of modification. For this purpose, it is convenient to employ homologous series of modifying agents: amines, aldehydes, imidates. Analysis of the type of dependence of the stabilising or destabilising effect on the chain length of the reagent has proved useful for the elucidation of the influence on the stability of proteins of integral parameters such as the surface hydrophobic character or surface charge.[66]

The influence of temperature on the stabilising or destabilising effects can sometimes help to elucidate[66] what type of interactions in the protein makes a decisive contribution to the stabilisation. In particular, if the stabilising effect increases with increase of temperature, then this is important evidence for the enhancement of hydrophobic interactions in the protein.

In conclusion of this Section of the review, we shall draw attention to the possibility of one fundamental error in the interpretation of experimental data. A particular mechanism of inactivation characteristic of the native protein can sometimes be significantly inhibited by chemical modification. For example, the thermal inactivation of bovine serum albumin in solution is sometimes caused mainly by its aggregation.[108] By introducing an excess negative charge on the protein surface (for example by citraconylation), aggregation can be fully prevented. The retardation of the inactivation observed experimentally in this case[108] is caused by a change in the inactivation mechanism and not by the internal stabilisation of the protein (due to its modification). In studies with modified and even with immobilised proteins or proteins modified by mutation, it is always important to make sure that the mechanisms of their inactivation are identical with the mechanisms for the native proteins.

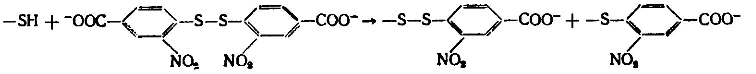
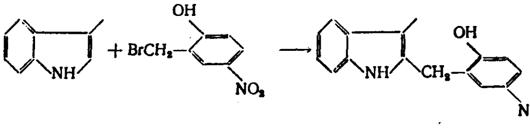
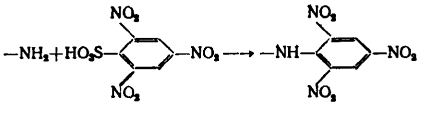
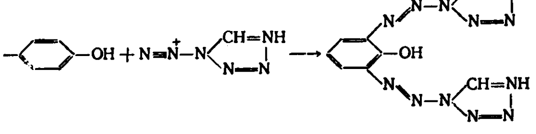
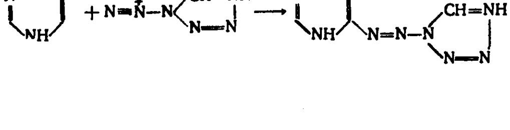
III. MOLECULAR CAUSES OF THE STABILITY OF PROTEINS

The principal molecular causes of the stability of proteins were recently analysed by the present authors.[19] Here we shall consider them only in order to elucidate whether nature has left provision (and what kind of provision) for the artificial increase of the stability of proteins.

1. The Binding of Metal Cations, Substrates, Prosthetic Groups, and Other Low-Molecular-Weight Ligands

The most general explanation of the facts concerning the stabilisation of enzymes in their interaction with ligands was given by Schellman.[109] There exist at least two states of protein—native and denatured, and any compound is in principle capable of binding to either one. The preferential binding to one of the forms of the protein inevitably stabilises it in relation to the other by the amount equivalent to the free energy of formation of the corresponding complex. It is known that the effectors of enzyme activity are bound in the region of the active centre or near it. The formation of the enzyme—ligand complex therefore requires that the protein exist in the native conformation; there is as a rule no binding to the denatured form. This is precisely why specific low-molecular-weight ligands usually stabilise proteins.[109]

Table 4. Spectrophotometric determination of certain functional groups in proteins.

Reaction	λ, nm	Molar absorption	Refs.
	412	13 600	[99]
	410	18 000	[100]
	420	13 000	[101]
	550	13 800	[102]
	480	20 500	[102]

In connection with the preparation of artificially stabilised enzyme preparation by interaction with effectors, we draw attention to the fact that in such interactions proteins frequently undergo conformational changes,[110] i.e. are converted into other, sometimes more stable conformations. An attempt must be made to fix this stable conformation, for example with the aid of immobilisation;[111] a critical analysis of this approach has been carried out in a review.[62]

2. Protein–Protein and Protein–Lipid Interactions

In vivo proteins frequently interact with other protein molecules, lipids, and polysaccharides.[112] The structures then formed can be divided arbitrarily into two fundamentally different types: firstly, complexes with a small number of either protein–protein contacts (for example, subunit enzymes[113] or species comprising proteases associated with protein inhibitors[114]) or protein–lipid contacts (such as the complexes of albumin with aliphatic acids[115]) and secondly systems with a large number of inter-related concerted contacts of different types (protein–protein, protein–lipid, lipid–lipid) of the kind which obtain, for example, in biological membranes.[116] The interaction of the protein with other molecules in both these and other types of structures can significantly increase its stability.

The mechanism of stabilisation on formation of individual protein–protein or protein–lipid contacts has been in principle understood.[114] Together with polar and charged groups, there are "hydrophobic clusters" on the surface of proteins and their contact with water is thermodynamically unfavourable. On formation of the complex, the lipid or protein molecule "sits" on this cluster and thereby prevents its contact with the solvent.[117] The observed free energy of stabilisation amounts to several kcal mol^{-1} per protein–protein contact.[113,114]

Such protein–protein or protein–lipid contacts can also be created artificially: in the presence of lipids[118,119] or high concentrations of proteins (for example, albumin),[120,121] the stability of certain enzymes increases appreciably.

The mechanism of the stabilisation of enzymes when the latter are enclosed in biological membranes appears less unambiguous. Indeed, together with the "shielding effect" discussed above, many other factors should play an important role in this instance. Among them, we shall specify in the first place a change in the rigidity of the protein molecule as a result of its multipoint interaction with other proteins and lipids and we shall consider the influence of this factor on stability.

3. The Rigidity of the Protein Molecule

The rigidity determines the ability of the macromolecule to assume different states in conformational space[122] and is related directly to the stability of the protein. Indeed, both the protein denaturation process (the manifestation of the instability of the protein) and the fluctuations about a certain statistical average stage (the manifestation of the "non-rigidity" or flexibility of the protein) are based on the same molecular mechanisms: the vibrational and rotational movement in the macromolecule. The difference between these processes consists only in the fact that in denaturation a cooperative conformational transition of the entire globule takes place,[26] while local fluctuations in the structure involve only individual sections of the globule without a significant alteration of the overall conformation.[123]

In the present review we shall not attempt to give a rigorous thermodynamic definition of rigidity[122,123] or to relate it to the thermodynamic parameters of the stability of the protein.[124] Undoubtedly many factors which determine the stability of the protein (in the first place hydrophobic interactions) influence also its rigidity.[122,124] Here we shall consider only one question: how a factor such as immobilisation—natural or artificial—affects the rigidity and stability of the protein?

In nature proteins and membranes exist in a naturally immobilised state; this must be understood as having the consequence that, as a result of interaction with other proteins and lipids, their rotational diffusion as well as their vibrational and rotational movement are significantly restricted. The degree of immobilisation of proteins in a membrane depends in many respects on the integrity of the membrane and on the degree of structural formation in the latter. When the latter parameter is altered (for example, in a phase transition within the membrane), the "degree of immobilisation" of proteins changes significantly,[125] which entails changes in the catalytic properties of membrane enzymes.[125,126] However, until recently there have been virtually no data concerning the influence of structure formation in membranes on the stability of membrane enzymes.

A pioneering study on these lines was carried out by Welker.[127] He grew the obligatory thermophilic strain *Bacillus stearothermophilus* at temperatures ranging from 55° to 70 °C and observed that, with increase of the growing temperature, there is a significant increase of the stability of the cell membrane (which he inferred from the decomposition of cell protoplasts at elevated temperatures—Table 5). Simultaneously with the strengthening of the structure of the membrane, there is a significant increase in the thermal stability of membrane enzymes; this has been noted both for peripheral alkaline phosphatase and integral NADH-oxidase (Table 5). An increase of stability is observed only for enzymes forming part of the composition of the membrane. After extraction from the membrane, the stability of alkaline phosphatase first falls sharply and then becomes independent of the temperature at which the given culture of microorganisms has been grown (Table 5). Thus these data confirm the earlier hypothesis[128,129] of the stabilising influence of the membrane structure on proteins.

Table 5. The influence of the growth temperature (T_g) of the culture on the properties of the membranes of the cells of *Bacillus stearothermophilus* and the thermal stabilities of the enzymes.[127]

T_g, °C	Disruption of protoplasts, %				Degree of inactivation, %					
					free A.P.*		membrane A.P.		NADH-oxidase	
	65°	70°	75°	80°	65°	70°	65°	70°	75°	80°
55	0	100	100	100	100	100	87	100	100	100
60	0	80	100	100	100	100	0	92	90	100
65	0	0	70	100	100	100	0	20	75	84
70	0	0	10	100	100	100	0	5	0	10

*A.P. = alkaline phosphatase.

Comparison of the thermal stabilities of enzymes immobilised by natural (in a biomembrane) and artificial (on a polymeric carrier) procedures is extremely instructive. Fig.1 presents the temperature dependence of the catalytic activity of the integral membrane enzyme NADH-oxidase.[127] Evidently the stronger the membrane in which the enzyme has been incorporated (i.e. the higher the temperature at which the culture has been grown), the higher the temperature optimum of the catalytic activity. A similar family of experimental curves has been obtained[130] for artificially immobilised trypsin, whose molecules were attached to the carrier by different numbers of bonds (Fig.2). We believe that the identity of the forms of the temperature variations in Figs.1 and 2 is not fortuitous. Apparently it reflects the same trend: the increase of the stability of the enzyme as a result of the strengthening of its structure. The difference consists only in the fact that the strengthening is achieved either as a result of more pronounced structure formation in the natural protein-lipid membrane matrix *in vivo* or via an increase in the number of bonds between the enzyme molecule and the artificial polymer matrix *in vitro*

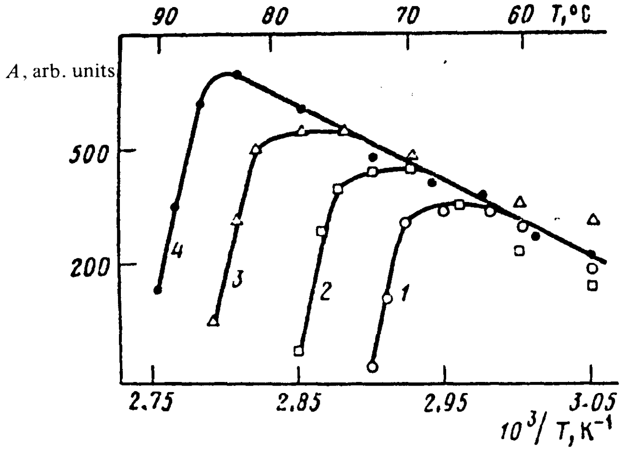


Figure 1. Temperature dependence of the catalytic activity (A) of a membrane enzyme (NADH-oxidase from the cells of *Bacillus stearothermophilus* grown at different temperatures): *1*) 55 °C; *2*) 60 °C; *3*) 65 °C; *3*) 65 °C; *4*) 70 °C.[127]

4. Salt Bridges

Among all the stabilising factors based on electrostatic interactions, ion pairs (or, in other words, salt bridges) make the greatest contribution to the stabilisation of protein.

There are relatively few ion pairs in proteins,[131,132] but they make a significant contribution to their stabilisation—up to 5 kcal mol^{-1} per ion pair if the latter is located within the globule and 1–2 kcal mol^{-1} if it is on the surface.[1,113] It is therefore not fortuitous that nature willingly makes use of them and creates thermophilic proteins with increased stability.[19]

We shall quote yet another example. Glyceraldehyde 3-phosphate dehydrogenase, from the moderate thermophile *Bacillus stearothermophilus* has a three-dimensional structure similar to that of the enzyme from rabbit muscle[133] with only a small but significant difference: in the region of subunit contacts, the thermophilic dehydrogenase has a cooperative system of additional salt bridges, which is missing from the mesophilic enzyme. This is in fact the main molecular reason why both the denaturation and the optimum catalytic activity of the thermophilic enzyme are observed at a higher temperature than for the enzyme from rabbit muscle.[133]

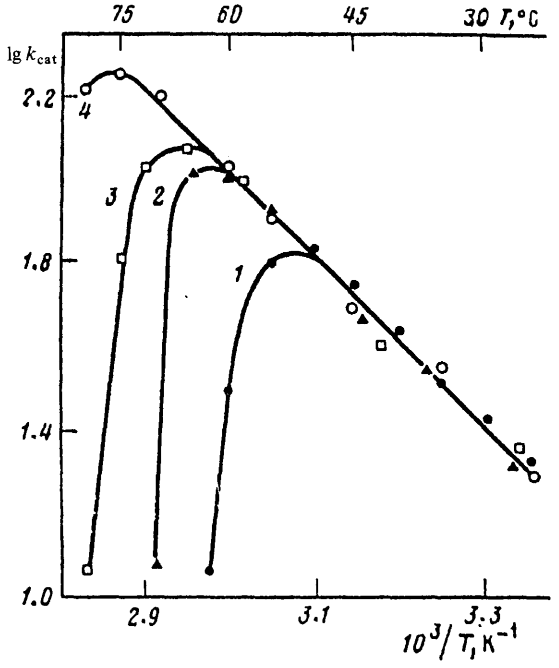


Figure 2. Temperature variation of the catalytic constants k_{cat} for the hydrolysis of the specific substrate catalysed by trypsin: *1*) free enzyme; *2–4*) enzyme immobilised covalently in polyacrylamide gel by 5, 8, and 15 bonds respectively.[130]

An attempt may be made to create in the protein additional ion pairs artificially, for example by site-specific mutagenesis or by chemical modification. However, success of such procedures, i.e. the appearance of a salt bridge, requires detailed knowledge about the steric structure of proteins. The likely usefulness of this approach will probably increase as more new information is obtained about the structure of proteins, in the first place by X-ray diffraction.[134]

5. Hydrogen Bonds

The hydrogen bonds in proteins play an important structural role; they maintain the spatial organisation in the secondary structures (α-helices, β-structures, rotations). It has come to be assumed that the formation of a hydrogen bond in proteins is an energetically favourable process. The energy of the hydrogen bond is frequently calculated as the result of two events: the dissociation of "old" hydrogen bonds between a polar atom (for example, the oxygen of the amide group) and a water molecule and the formation of "new" hydrogen bonds between the polar atoms in the protein molecule and has been estimated as 1–2 kcal mol^{-1}. However, in this treatment no account is taken of the fact that there is a parallel thermodynamically unfavourable process involving the immersion of the polar atom or group (for example, the amide group) within the hydrophobic nucleus of the globule. Allowance for the energetics of this process leads to the conclusion that[1] the free energy of formation of the hydrogen bond in the protein is close to zero. In other words, the hydrogen bond is the price which the protein has to pay for the characteristic features of its structure. In our view, there is therefore no point in attempting (for example, by methods of protein engineering) to introduce hydrogen bonds into the protein artificially.

6. Disulphide Bridges

The ideas about the stabilisation of proteins with S–S bonds arrived in protein chemistry from polymer chemistry. In the middle 1950's, it was shown that[135,136] the intramolecular cross-linking of macromolecules imparts to them additional rigidity and increases their stability. The nature of this stabilisation is entropic:[135] as a result of the appearance of a cross-link in the macromolecule (a S–S bond in a protein), there is a significant decrease in the entropy of the open-chain form, which entails an increase in the free energy difference between the native and denatured states of the protein. This stabilising contribution in proteins amounts to up to 4–5 kcal mol^{-1} per S–S bond.[137]

Modern methods of protein chemistry lead to extensive possibilities for the introduction of intramolecular cross links into proteins. Firstly, one can use bifunctional modifying agents.[133] The methods developed for the imposition of "molecular yokes" make it possible in the main to cross-link surface regions in the protein. Another approach involves the introduction of a cross link within the protein molecule. Here the method of site-directed mutagenesis can serve as the instrument. For example, it has been possible to introduce S–S bonds into lysozyme T4—a protein from which they are absent—by this method.[139]

7. The Low Content of Aminoacids Susceptible to Oxidative Modification

One of the common mechanisms of the inactivation of proteins involves the oxidation (for example, at an elevated temperature) of aminoacid residues important for the structure.[12,13] In the first place the SH group of cysteine and the indole ring of tryptophan undergo oxidative modification. It is therefore not fortuitous that the highly stable thermophilic proteins contain much smaller amounts of these labile aminoacids (in the first place Cys).[19]

Apparently there exist two pathways to the stabilisation of enzymes unstable with respect to oxidation. The first involves a copy of the procedure which nature has used in thermophilic enzymes: to decrease the number of SH groups. For this purpose, one has to attempt by the method of site-specific mutagenesis to replace the Cys residues, most susceptible to oxidation (provided of course that they are not involved in catalysis), by others less labile, but having similar properties (geometry, hydrophobic properties).[140] The other procedures are methodologically simpler: to create around the enzyme a microenvironment which would shield it from the inactivating factor (oxygen). For example, a charged polyelectrolyte can serve successfully as a shield of this kind: it "coats" the enzyme and significantly hinders the access of oxygen to it. The "salting out" of oxygen by the polyelectrolyte matrix made it possible to increase the stability of labile hydrogenases by a factor of thousands.[141]

8. Compact Packing of Aminoacid Residues

The protein molecule in solution represents a compactly packed structure; the packing density of aminoacid residues in the globule is close to that characteristic of crystals of organic molecules.[1] Nevertheless, there exist "cavities" within the protein which are filled with water molecules (5–15 molecules per protein with a molecular weight of 20 000–30 000). The contact between the polar water molecules and the hydrophobic nucleus of the protein is thermodynamically unfavourable and destabilises the protein.

The stability of the protein can be in principle increased by further compaction, i.e. by the "additional compression" of the protein structure with simultaneous removal of water molecules from the internal region. This type of procedure has been used by nature to create thermophilic enzymes; in their structures, certain internal aminoacid residues have been replaced (compared with the corresponding mesophilic analogues) by more bulky residues.[19] The idea of the compaction of the protein can also serve as the basis for artificial stabilisation if an attempt is made to replace suitable aminoacid residues, for example, by site-directed mutagenesis. It is then necessary to bear in mind that the replacement of aminoacid residues by certain others is impermissible, because it can lead to serious infringements of the protein structure.[142]

9. Hydrophobic Interactions

At the present time ideas about the nature of hydrophobic interactions and their role in the stability of proteins have been arranged to form an elegant system.[143–145] In proteins, about half of the entire volume is occupied by aminoacids with non-polar side groups. Their contact with water is thermodynamically unfavourable, because the introduction of a non-polar fragment into water makes the structure of the latter more ordered. Such structure formation in water diminishes the entropy of the system and hence increases its free energy.# Therefore, in the organisation of the structure of the protein (coiling), the following tendency is manifested: to remove from contact with water the greatest possible number of non-polar fragments in the protein and to hide them in the bulk of the globule.[147] The influence of the unfavourable entropy factor is thereby weakened, hydrophobic interactions are intensified, and the stability of the protein increases.§

As soon as the idea of hydrophobic interactions as a factor stabilising the protein arose, attempts were made to correlate the stability of the protein with its hydrophobic properties. For this purpose, it was natural to attempt the determination

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#Structured clusters of water molecules were previously detected only around very small organic molecules.[143] In the X-ray diffraction analysis of the membrane protein crambin, it has recently been possible to observe a pentagonal cluster formed by water molecules around a non-polar fragment of the protein surface.[146] Thus it was demonstrated for the first time that the protein molecule does not alter qualitatively the character of the interaction of the non-polar fragments with water, i.e. the hydrophobic interactions have the same (entropic) nature for both small molecules and macromolecules.

§ This point of view on the entropic nature of hydrophobic interactions is dominant at the present time but is not the only one—see, for example, Hvidt's review.[148]

of a quantitative criterion of hydrophobic character. Tanford and co-workers suggested[149-150] that the free energy of the transfer of aminoacids from water to the organic phase be used. According to this classification, the more negative the ΔG of the transfer process for the aminoacid, the more hydrophobic it is (Table 6). The creation of a quantitative scale of hydrophobic character stimulated the search for correlations between the stability of the protein and its overall hydrophobic character, calculated as the sum of the hydrophobic character of all its constituent aminoacids. However, unambiguous conclusions could not be obtained from the correlations both for mesophilic proteins[28-30] and on comparing thermophilic and mesophilic proteins.[154,155]

Table 6. Indices of the hydrophobic character of aminoacids.

Amino-acid	ΔG for transfer, kcal mol^{-1}*	f, %**	Hf, arb. units***	Amino-acid	ΔG for transfer, kcal mol^{-1}*	f, %**	Hf, arb. units***
Trp	−3.77	0.27	12.95	His	−0.87	0.17	12.84
Phe	−2.87	0.50	13.43	Thr	−0.07	0.23	11.65
Tyr	−2.67	0.15	12.29	Ser	−0.07	0.22	11.26
Ile	−3.15	0.60	14.77	Asn	−0.09	0.12	11.00
Leu	−2.17	0.45	14.10	Gln	0.00	0.18	11.28
Val	−1.87	0.54	15.07	Asp	−0.66	0.15	10.97
Pro	−2.77	0.18	11.19	Glu	−0.67	0.07	11.19
Ala	−0.87	0.38	12.28	Lys	−1.64	0.03	10.80
Met	−1.67	0.40	14 33	Arg	−0.85	0.01	11.49
Cys	−1.52	0.50	14.93	Gly	−0.10	0.36	12.01

*The free energy of transfer from water to the organic solvent.[151]

**The fraction of the residues hidden within the globule.[152]

***The hydrophobic character of the environment in proteins.[153]

In the first part of the review, we already noted one of the causes of the failure of this approach: unduly small differences between the stabilities of the proteins against the background of large differences in their structures.

Another cause is that, when the aminoacid composition is determined by aminoacid analysis, one finds as a rule the overall contents of Asp + Asn and Glu + Gln, i.e. the acid and the corresponding amide, and one does not take into account the form in which these aminoacids are present. On the other hand, the differences between the hydrophobic properties of the acid and amide forms are large (cf. Asp and Asn, Glu and Gln in Table 6). For example, the highly stable ferredoxin *Clostridium thermosaccharolyticus* has a stability differing from that of the usual protein from *Clostridium tartarivorum*,[156] which has a normal stability, only by the fact that Glu residues are located in positions 31 and 44 and not Gln. With the aid of the usual amino-acid analysis, this difference could not be revealed. The comparison of X-ray diffraction data for the two proteins enabled the authors to resolve this problem.[156]

We may point to yet another source of error which arises in the analysis of correlations between the overall hydrophobic character and the stability of proteins. Sometimes the hydrophobic character of a stable thermophilic protein is compared with that of a statistical-average mesophilic protein and not a less stable mesophilic homologue.[157] This is methodologically absolutely incorrect; for a discussion of this question, see the review of Mozhaev and Martinek.[19]

The question arises whether there is any point (even when all the factors have been taken into account and a comparison made correctly) in seeking correlations between the stability and the overall hydrophobic character of proteins. Such a correlation would apparently be valid only for a certain "idealised" protein (it is sometimes represented by a drop of oil separated from contact with the solvent by a palisade of polar and charged groups[158]). Indeed, in such a hypothetical protein all the non-polar aminoacids would be involved in hydrophobic interactions. Although this simplified picture reproduces correctly the general trend towards the intensification of hydrophobic interactions in proteins, it is not observed in practice. According to X-ray diffraction data, approximately 50% of the area of real proteins is occupied by non-polar aminoacids.[114,145,147,159] They are frequently organised into surface hydrophobic clusters.[145] This has a functional importance because it enables proteins to bind via hydrophobic interactions to other proteins (polyenzyme complexes), lipids (biological membranes), polysaccharides (cell wall), and substrate effectors (enzyme catalysis and its regulation), i.e. ultimately it enables them to function correctly.[160,161] However, in proteins in the free, unbound state (enzymologists have to deal most often precisely with such objects), the disposition of non-polar aminoacids on the surface is "harmful" for stability, because it leads to the loss of free energy as a result of the weakening of hydrophobic interactions.

The non-ideality of protein structure (from the standpoint of the maximum realisation of hydrophobic interactions in them) necessitated the search for new approaches to the definition of a scale of the hydrophobic character of aminoacids. It became evident that the scale[149,150] established on the basis of the extraction model reflects incorrectly many trends in the coiling of the protein. It was therefore suggested that the hydrophobic character of aminoacids be estimated from statistical data for their distribution in the steric structure of proteins.[152,153,162,163]

Chothia's statistical scale[152] reflects the distribution of aminoacids in the bulk of the protein globule: the more frequently is the aminoacid encountered within protein globules and the more rarely on the surface, the more hydrophobic it is thought to be. Another statistical scale, set up by Ponnuswamy and co-workers,[153] is based on the fact that the hydrophobic character is determined by the microenvironment in which the given aminoacid residue is present. In this case the aminoacid which is surrounded by more hydrophobic neighbours in the protein globule is regarded as the more hydrophobic. The hydrophobic character of the microenvironment is then regarded as the sum of such characters[149,150] in the nearest neighbours in the tertiary structure of the aminoacids.

Comparison of these two statistical scales of the hydrophobic character[152,153] shows (Table 6) that they agree fairly well despite the fact that they are based on different principles. Thus in both scales Ile, Val, and Cys are the most hydrophobic and Lys, Arg, Asp, Glu, Asn, and Gln are the least hydrophobic. On the other hand, appreciable discrepancies between the data derived from the statistical scales and the extraction (Tanford) scale are observed. Thus Trp, which is the most hydrophobic on the extraction scale, occupies an intermediate position on the statistical scales and Tyr and Pro, which are closest to it in terms of their hydrophobic properties, should be more properly assigned to hydrophilic aminoacids in terms of the statistical scales.[152,153]

The causes of these discrepancies were first analysed by Chothia,[152,159] who concluded that the introduction of a polar atom into the aminoacid diminishes its hydrophobic character by 1–1.5 kcal mol^{-1}. It is therefore not fortuitous that the aminoacids which are most hydrophobic on the extraction scale (Trp and Tyr) do not belong to the most hydrophobic aminoacids on the statistical scales (Table 6). Although their large surface area ensures their high hydrophobic character, the presence of a polar atom makes their presence within the protein globule significantly less favourable.

There exist also other causes of the discrepancies between the extraction[149,150] and statistical scales of the hydrophobic property.[152,153] A classification based on the extraction properties has been established solely on the basis of model experiments (transfer of the given substance from the aqueous to the organic phase) and therefore it in no way takes into account the fact that the aminoacids considered in fact enter into the composition of the polypeptide chains. In other words, in real proteins they must adjoin other aminoacids which in principle influence the geometry and energy of their neighbours.[164] Furthermore, the principle of close packing is realised in proteins[1,140,147] and therefore on coiling the most bulky aminoacids (Trp and Tyr) they are forced to remain on the surface of the globule in order not to infringe the compactness of the structure.

Thus there are three main factors which prevent the realisation of hydrophobic interactions in the proteins with the maximum advantage for the stability of the steric structure. Firstly, there is the need to ensure a sufficiently close packing of the aminoacids in the protein. Secondly, the geometry and energy of aminoacids are influenced by the microenvironment, i.e. they are neighbours in the tertiary structure. Thirdly, hydrophobic clusters, which *in vivo* ensure the interaction of the protein with other molecules, should remain on the surface of the protein when it is coiled up. Consequently, there is hardly any point in attempting to find a correlation between the stability of the protein and its overall hydrophobic character. It has been suggested[154] that the content of aliphatic aminoacids be used as a more suitable parameter, because they are indeed more frequently encountered within the protein than on the surface. The so called aliphatic protein index has been defined:[165]

$$A = X_{\mathrm{Ala}} + aX_{\mathrm{Val}} + b(X_{\mathrm{Ile}} + X_{\mathrm{Leu}})\,.$$

where X_{ala}, X_{Val}, X_{Ile}, and X_{Leu} are the mole fractions of Ala, Val, Ile, and Leu in proteins and a and b are numerical coefficients determined by the size of the aminoacid residues. Fig.3 shows that the aliphatic index of the more stable proteins from thermophilic organisms is indeed higher than that of mesophilic proteins.

The following characteristics of the relation between the hydrophobic interactions in proteins with enhanced stability follow from the data considered. In the most general form, one may say that the increase of stability of proteins *in vivo* (for example of the stability of thermophilic enzymes) occurs not only and not so much at the expense of the increase of the overall hydrophobic character[166] as due to the more "correct" disposition of the non-polar aminoacids in the globule.[167] In other words, the greater the number of non-polar protein fragments are hidden in the interior of the globule and the smaller their number exposed to the solvent, the greater the stability of the protein. This picture has been described quantitatively by Lee and Richards,[147] who introduced the concept of the "surface area accessible (to the solvent)". It has been known that[159] the decrease of the overall free energy of the hydrophobic interactions in the protein ΔG_h depends on the change in the accessible surface area ΔA_s in the following manner:

$$\Delta G_h = \sigma\,\Delta A_s\,,$$

where σ is a proportionality coefficient numerically equal to approximately 25 kcal mol^{-1} A^{-2}. It follows from this equation that the decrease of the surface area of the hydrophobic contact with water should entail the intensification of the internal hydrophobic interactions in the protein and hence should stabilise the latter. This is indeed observed on comparing thermophilic enzymes with the corresponding mesophilic enzymes,[168,169] on comparing the structures of a series of mesophilic homologues,[170] and also from the analysis of the stability of proteins modified by mutation.[161,171]

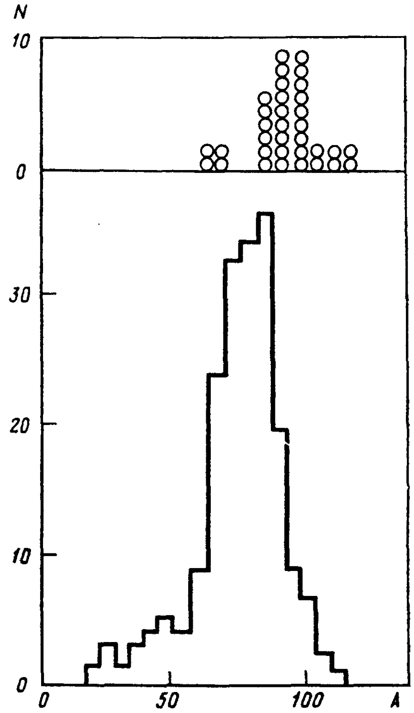

Figure 3. Distribution of the aliphatic index (A) among 34 proteins from thermophilic bacteria (upper section of the Figure) and 208 proteins from mesophilic organisms (lower section);[165] N = number of proteins.

Summarising this Section we may note that the stabilisation of proteins by the intensification of the hydrophobic interactions in them constitutes an extremely promising practical approach.[19,161] One should attempt either to decrease the hydrophobic character of the surface of the protein or to enhance its internal hydrophobic character.

IV. ARE THERMOSTABLE CATALYSTS NEEDED FOR BIOTECHNOLOGY?

The application of thermostable biocatalysts in biotechnolog has a number of advantages.[14-17,172]

The gain in the rates of processes. According to the van't Hoff rule, on raising the temperature by 10 K the rates of chemical, including enzyme-catalysed, reactions increase on average by a factor of 2–3.

The possibility of a shift of the thermodynamic equilibrium. The position of the chemical reaction equilibrium depends on temperature. According to the Le Chatelier principle, by raising the temperature, it is possible to displace the equilibrium towards synthesis for those reactions which take place with absorption of heat (endothermic reactions). Unfortunately, the thermochemistry of enzyme reactions which are of practical value has so far been studied in inadequate detail. As an example of an important reaction whose equilibrium shifts in an unfavourable direction on raising the temperature, we may quote the formation of a peptide bond.[173] Indeed, it has been shown that,[174] only by reducing the temperature for chymotrypsin-catalysed peptide synthesis, is it possible to increase the yield of the final product—the dipeptide.

The increase of the duration of work of the biocatalyst. The biotechnological processes actually introduced into practice involve a high economic cost contributed by the enzymes themselves.[175,176] Evidently the stabilisation of enzymes makes it possible to reduce this cost by increasing the period during which they can be used.

High resistance to other denaturing influences. As a rule, enzymes resistant to the action of high temperatures manifest an increased resistance also to other denaturing influences: concentrated solutions of denaturing agents, extreme pH values, and degradation by proteases. This is true, for example, of natural thermostable enzymes from thermophilic micro-organisms.[177,178] The practical value of this universal stabilisation is high, since the enzymic transformations of many natural compounds and the preparative synthesis of many substances can be effected in the required direction only in organic solvents or in aqueous organic media with a high content of the organic component.[179,180]

Increase of the efficiency of the catalytic process as a result of the increase of the solubility and volatility of the reactants and the decrease of the viscosity of the solutions at elevated temperatures. With increase of temperature, the solubility of the initial reactants increases also as a rule, which makes it possible to work with their more concentrated solutions and, in conformity with the Law of Mass Action, the absolute yield of the final product can be increased. If as a result of heating it has been possible to increase significantly the volatility of one of the final products, then the equilibrium in the synthetic reactions is strongly displaced towards the final product and their yield therefore increases. The decrease of viscosity on heating makes it possible to accelerate and hence to increase the efficiency of the processes in the kinetics of which diffusion plays a significant role.

Sterilisation of the products in the course of the reaction and decrease of the probability of the microbial infection of the reactors. The latter factor must always be reckoned with when biotechnological processes are carried out and its role can be as a rule significantly reduced at elevated temperatures.

The process can be readily arrested by simple cooling. However, experiments at elevated temperatures also suffer from certain disadvantages. One of these is the increase of the rate of certain side processes, in the first place high-temperature oxidation[13] and racemisation of aminoacids and their derivatives.[181] The economically justified selection of conditions, high-temperature or low-temperature, therefore constitutes a problem which has an independent solution for each specific case.[182]

V. METHODS OF PREPARATION OF STABLE ENZYME CATALYSTS

1. The Search for Enzymes with Increased Thermal Stability in Mesophilic Sources

This approach is the oldest, traditional, and apparently does not require special comment. Its logical development has been the search for enzymes in sources which by their very nature are adapted to existence under high-temperature conditions.

2. Isolation of Enzymes from Thermophilic Sources

A homogeneous preparation of a thermophilic enzyme was first obtained 25 years ago.[183] Since then, the advantages of the use of thermophilic enzymes in biotechnology have been frequently discussed. Apart from the advantages of the thermally stable biocatalysts which were described above and which apply equally to thermophilic enzymes, we shall mention one other. Thermophilic micro-organisms are preferable to mesophilic organisms from the microbiological standpoint. Thus widescale cultivation of thermophilic strains is frequently cheaper than the cultivation of mesophilic strains owing to the decrease of the energy expenditure (there is no need to cool the growing biomass).[172] It is also important that, although thermophilic enzymes are very stable, they have not attained the absolute limit of thermal stability: there exists a certain reserve for additional stabilisation. Thus, having immobilised a thermophilic asparaginase[172] and protease, it has been possible to increase by a factor of 10 the resistance of these enzymes to irreversible thermal inactivation, which was in any case already high without this step.

Nevertheless there is virtually no information in the literature about the use of thermophilic enzymes in biotechnological practice. In our view, this is associated with the fact that, although the maximum catalytic activity of thermophilic enzymes is attained at higher temperatures (by 20–40 K), the activities of the mesophilic and thermophilic enzymes themselves are frequently identical at the temperature optimum.[48,169,185–188] Reports stating that the catalytic activity of a thermophilic enzyme at the temperature optimum is higher than that of the corresponding mesophilic enzyme have been appearing only occasionally.[189]

Not only are the catalytic activities of the thermophilic and mesophilic enzymes equal at the temperature optima but their thermal stabilities are also similar.[169] Thus, when thermophilic and mesophilic enzymes are compared, a correlation is manifested which is the same as that observed previously[190–194] for mesophilic proteins: the higher the catalytic activity, the lower the stability of the protein. In other words, having attained a greater stability, thermophilic enzymes have to sacrifice their catalytic activity partially.[187]

On the other hand, thermophilic enzymes have a property which makes them irreplacable for the purposes of biotechnology: the ability to alter their substrate specificity when the temperature is varied. This property is manifested particularly strikingly in the enzymes (proteases, nucleases, etc.) which act on high-molecular-weight substrates. The reason for this is that the substrates themselves (i.e. proteins and nucleic acids) undergo temperature-dependent conformational changes;[195] other new peptides and nucleotides bonds of the substrate are then exposed to the solvent and become accessible to the action of the enzymes. The appearance of a new specificity[196] is apparently of interest for the vigorously developing genetic engineering, which requires a set of restrictases with different specificities.[197] One may hope that thermophilic restrictases will become new and highly effective instruments in genetic engineering.

3. Synthesis of Highly Stable Enzymes for the Introduction of a Thermophilic DNA into a Mesophilic Culture

Towards the end of the 1970's, reports appeared[198-200] that the introduction into the cell of a mesophilic organism (for example, *Bacillus subtilis*) of DNA from a related thermophilic organism (for example, *Bacillus caldolyticus*) results in the transformation of the mesophilic culture into the thermophilic culture at an elevated temperature. The transformant then loses its ability to grow at the usual temperature but acquires a new property—the ability to grow at an elevated temperature.[198] The entire biosynthetic apparatus of the transformant then acquires an increased thermal stability[198,199] and the synthesis of highly stable enzymes begins in the cell.[200]

At the beginning of the 1980's, another version of the genetic approach began to be used:[201,202] instead of a whole molecule of thermophilic DNA, only its fragment—the gene coding a specific protein—is introduced into the mesophilic culture. This approach has the undoubted advantage that the required stable enzyme can be obtained with a high yield (actually tens of times greater than in its isolation from a thermophilic culture).[202] Another advantage is that the operations involved in the isolation and purification of the protein are significantly simplified. Indeed, because at the elevated temperature almost all proteins synthesised by the mesophilic culture with the exception of the required high-stable protein are denatured, it is possible to achieve a high degree of purification of the protein at the expense of a small expenditure of time and at a small cost in equipment.

4. The Protein Engineering Method

At the beginning of the 1970's, successful experiments designed to create recombinant DNA were first carried out.[203] It became clear that a new powerful instrument for the wide-scale preparation of natural products and the synthesis of biological molecules with a broad spectrum of properties which do not exist in nature had been placed in the hands of investigators. A new scientific-engineering field was created on this basis—genetic engineering. By genetic engineering, one normally understands the construction *in vitro* of functionally active genetic structures (recombinant DNA), their introduction into cells, and the subsequent biosynthesis by the cells of biological molecules which are not characteristic of them. At the present time the advances in genetic engineering both in our country[204] and abroad[205,206] are generally recognised and the prospects are hopeful.

We shall deal with only one version of the genetic-engineering approach—site-directed mutagenesis[54-58] or "protein engineering".[20] This method makes it possible to obtain modified proteins differing from the prototype proteins by the replacement of, for example, only one aminoacid residue in a specific position in the protein structure. For biotechnology, the method is of interest primarily because it makes it possible to alter specifically the structure of enzymes, their catalytic properties, and their stability.[20] We shall now consider how this is done.

In the first place we shall deal with the primary structure of the initial enzyme[103] and then with its tertiary structure.[134] Then the following stage becomes possible—the selection of the site where the aminoacid residue is to be replaced. This stage does not involve any laborious operations, such as the growing of protein crystals, the determination of the aminoacid sequence, or the interpretation of X-ray diffraction patterns, which have to be performed in the next stage. However, this is in fact the key stage, because it determines the properties of the final product. Next, it is necessary to proceed from the language of protein structure (the aminoacid sequence) to the genetic code. For this purpose, an oligopeptide fragment (4–6 aminoacid residues) in the primary structure of the protein, at the centre of which is located the aminoacid to be replaced, is selected, and an oligodeoxyribonucleotide containing 12–18 bases coding the aminoacid sequence in the chosen oligopeptide, is synthesised.[210] The mutation is programmed in precisely this stage: instead of the nucleotide triplet coding the "native aminoacid", another triplet, coding the new (planned in the preceding stage) aminoacid residue, is introduced into the synthetic oligonucleotide by chemical synthesis. The subsequent operations reduce to genetic-engineering manipulations. Firstly, one finds (or creates artificially) a single-stranded plasmid incorporating the genes coding the given protein. Secondly, using DNA-polymerases and DNA-ligases, one creates enzymically, on the basis of the single-stranded plasmid and the nucleotide synthesised, a heteroduplex double-stranded plasmid. The oligonucleotide then initiates the synthesis of a double-stranded region, fulfilling the role of a seed. Since homoduplex plasmids together with heteroduplex plasmids are synthesised on single-stranded DNA molecules as templates, they are separated using different resistances to heating of homoduplex and heteroduplex plasmids. The heteroduplex double-stranded plasmids are then introduced into a convenient host cell in which they are transformed into two homoduplex plasmids: one contains the gene of the native protein and the other that of the mutant protein. The two genes and their subsequent cloning are carried out at the cellular level. The final result of the multistage process is transformant cells in which the mutant protein, differing from the initial protein by the replacement of one aminoacid residue at a rigorously specified site, is biosynthesised.

The method of site-specific mutagenesis appeared at the beginning of the 1980's and only the first steps have been taken.[20,207] Nevertheless, even the first achievements of the method are striking. We shall consider some of them concerning the synthesis of stabilised proteins.

In the molecule of lysozyme of the T4 phage there are no S–S bonds, but two SH groups are present. One of them, belonging to the Cys-97 residue, is located in the vicinity of the N-terminal region in the tertiary structure. The Ile-3 residue was replaced by cysteine by protein engineering. Since in the tertiary structure of the mutated lysozyme the Cys-3 and Cys-97 residues adjoined one another, the S–S bond was formed in a weakly oxidising medium. The conformations of the native and mutated enzymes were identical but their catalytic properties were different.[139] However, the lysozyme modified by mutation differs from the native protein by a significantly higher thermal stability (Fig.4). The reason for such stabilisation lies in the strengthening of the structure of the protein as a result of the introduction of the S–S bond.[139] Indeed, if the S–S bond in the modified lysozyme is cleaved, then the stability of the protein becomes virtually indistinguishable from that of the initial protein (Fig.4).

Another example of mutation designed to increase stability is provided by the α-subunit of tryptophan synthase. Several forms of the enzyme, differing from one another by the replacement of the aminoacid residue Glu-49 located in the hydrophobic nucleus of the globule by another aminoacid, were obtained.[208] Such changes do not alter either the conformation or the functional activity of the α-subunit of tryptophan synthase. However, the protein proves to be more stable the more hydrophobic aminoacid has been introduced in position 49. It follows from the correlation illustrated in Fig.5 that the method of site-specific mutagenesis provides unique possibilities for increasing the internal hydrophobic character (and hence the stability) of the protein by replacing polar aminoacids by more hydrophobic aminoacids. It is then naturally necessary to make specially sure that these replacements do not disrupt the compact packing (conformation) of the protein.

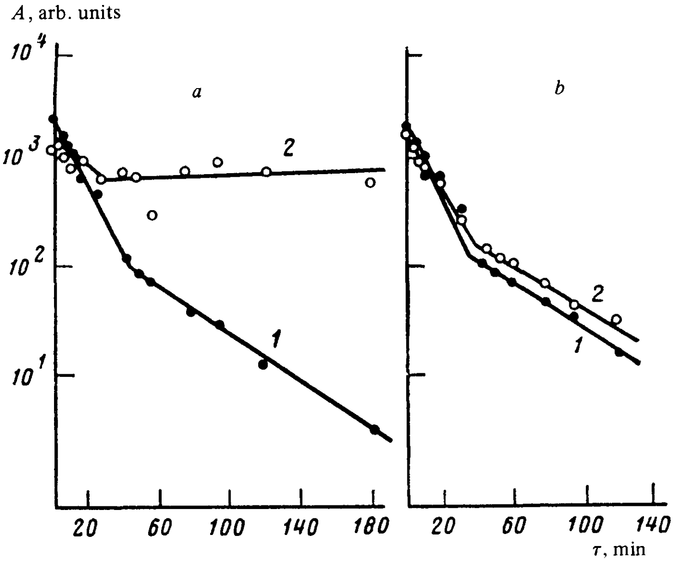

Figure 4. Kinetics of the thermal inactivation of the T4 lysozyme from a wild strain (curves *1*) and the T4 lysozyme with the substitution Ile-3 → Cys and subsequent oxidation with sodium tetrathionate (curves *2*) in the absence (*a*) and presence (*b*) of 10 × 10^{-3} M β-mercaptoethanol;[139] A = catalytic activity.

An example of the way that proteins resistant to oxidative inactivation can be obtained by the method of site-specific mutagenesis is provided by the study of Estell et al.[209] The Met-222 residue in subtilisin, which is located in the region of the active centre, readily enters into oxidative reactions, which inactivate the enzyme. It was replaced by the method of protein engineering by other residues, whereupon the activity of the enzyme did not diminish very greatly (within the limits of a factor of 10) but its resistance to inactivation by H_2O_2 increased significantly (Fig.6). The stabilisation is caused by the fact that, having removed from the active centre the readily oxidisable Met residue (having replaced it by other residues less susceptible to oxidation, namely Ser, Ala, and Leu), it proved possible to eliminate the very cause of oxidative inactivation.[209]

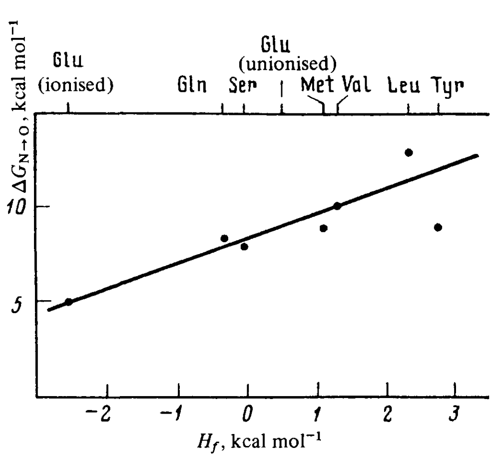

Figure 5. Dependence of the free energy of the stabilisation $(\Delta G_{N \to D})$ of the native conformation of the α-subunit of tryptophan synthase from *Escherichia coli* on the hydrophobic character (H_f) of the aminoacid residue in position 49;[208] the numerical values of the hydrophobic character of the aminoacids are based on Tanford's data.[150]

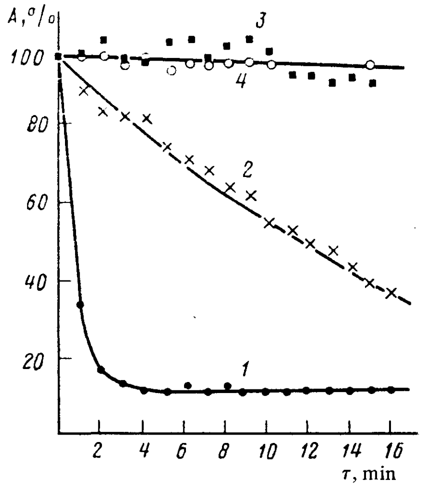

Figure 6. Kinetics of the inactivation (on treatment with 1 M H_2O_2) of subtilisin of a wild type (curve *1*) and mutant forms where position 222 contains the Cys (curve *2*), Ala (curve *3*), or Ser (curve *4*) residues;[209] A = catalytic activity.

However, the procedures of protein engineering are not simple. Successful work in this field requires the cooperation of specialists in the structure and chemistry of proteins and nucleic acids, in molecular and cell genetics, and in other branches of biochemistry and molecular biology. The work must be carried out at the highest experimental level using the latest advances in these fields and requires a large material expenditure. For this reason, traditional methods such as immobilisation and chemical modification, which have long been used to stabilise enzymes, still compete successfully with protein engineering.

5. Immobilisation of Enzymes

A series of special reviews have been devoted to the creation of stabilised enzyme preparations by the immobilisation method.[14–19] Here we shall therefore deal only with the main advances in the immobilisation approach.

As early as 1954, Lumry and Eyring formulated[211] the general ideas concerning the inactivation of enzymes, which still remain valid.[12,13] It was suggested that the inactivation be regarded as a two-stage process:

$$N \rightleftarrows D \rightarrow I$$

where N, D, and I are respectively the native, reversibly denatured, and irreversibly inactivated forms of the enzyme. Any inactivation begins as a rule with a reversible conformational change (the $N \rightleftarrows D$ stage in the scheme), which frequently embraces the entire globule. The reversible uncoiling stage is followed by irreversible processes ($D \rightarrow I$ in the Scheme), such as aggregation,[212] covalent modification of the aminoacid residues,[12,13] and irreversible conformational changes.[213–215]

The general approach to the stabilisation of enzymes based on the immobilisation method consists in a significant retardation or suppression of the primary uncoiling of the protein molecule (the $N \rightleftarrows D$ stage in the Scheme).[216] The multipoint addition of the protein molecule to the surface of a carrier proved to be the most fruitful for this purpose.[217,216] This immobilisation approach made it possible to retard by factors of hundreds and thousands both reversible[130,219] and irreversible[217,218] thermal inactivation of enzymes, their reversible uncoiling under the influence of chemical reagents,[220] and the dissociation of oligomeric fragments into subunits (see the literature references in the review of Arens et al.[216]).

The immobilisation approaches also proved to be extremely useful for the suppression of irreversible secondary processes (the $D \rightarrow I$ stage in the Scheme). Thus, if the inactivation is caused by protein–protein interactions (aggregation or autolysis), then, having immobilised the enzymes, such inactivation can be as a rule fully prevented (see the relevant reviews[14–17,62]). Immobilisation also helps to protect enzymes from inactivation by chemical modification. Such protection is achieved in two ways. Firstly, the enzyme is immobilised within a carrier, which "shields" it from contact with the inactivating molecules. An example of this approach is provided by the protection against oxidative inactivation of hydrogenases incorporated in polyelectrolyte carriers.[118] Secondly, a carrier containing functional groups competing for the inactivating substance or causing its decomposition is selected for immobilisation. For example, if the inactivation takes place under the influence of peroxy- or superoxide radicals, then, in order to achieve protection against them, the enzyme is immobilised jointly with peroxidase or catalase, which catalyse the decomposition of these radicals.[13]

6. Chemical Modification of Enzymes

The first successful studies on the stabilisation of enzymes by their chemical modification were carried out[221] in the middle 1950's. However, the view is still being encountered[65] that it is hardly possible to formulate sufficiently general rules whereby stabilised enzyme preparations can be obtained by chemical modification. Analysis of the numerous studies in this field (see the relevant reviews[18,64–66]) enabled us to reach certain conclusions about the causes of the stabilisation of proteins by their covalent modification.

As a result of the modification, the protein is sometimes converted into a more stable conformation different from the native conformation.[104,105]

Stabilisation takes place on modification of "key" functional groups[64] (they are also referred to as type II groups[66]).

New functional groups, introduced into the protein as a result of chemical modification, are capable to forming additional hydrogen bonds or salt bridges.[222]

Chemical modification by non-polar compounds intensifies the hydrophobic interactions in proteins.[223]

The hydrophilisation of the surface groups of the protein decreases the area of unfavourable contact of the outer hydrophobic residues with water.[19]

The question arises which of the mechanisms enumerated can be used as the basis of general approaches to the stabilisation of enzymes.

1. There is hardly any point in attempting to convert the protein by covalent modification into a more stable conformation different from the native conformation. The point is that the character of the conformational changes introduced by the modification is unpredictable in the vast majority of cases.

2. We shall consider the concept of "key functional groups".[64] The experiment involving chemical modification frequently looks as follows: the stability of the protein does not change with increase of the degree of modification until the attainment of a critical value, whereupon the stability increases sharply.[224] The observed variation is explained as follows:[64,66] for low degrees of modification (in the presence of a small excess of the modifying reagent), mainly the functional groups of the protein which are located on the surface and do not play an important role in the structure and stability are involved. However, in the presence of a large excess of the modifying agent, certain functional groups in deeper layers of the protein globule are modified. The modification of these groups, called "key" groups, improves the balance between the intramolecular interactions in the protein and stabilises the latter.

The application of the idea involving the modification of "key" functional groups in the protein encounters, however, a number of difficulties. The main one is how to discover which functional groups are the "key" groups. This is hardly possible to achieve *a priori*, for example, on the basis of the steric structure of the protein. The only reasonable procedure is to determine them empirically, i.e. by studying the dependence of the stability of the protein on the concentration of the modifying agent (degree of modification). Such studies must be carried out with exceptional care, because there exists a real risk of "overlooking", missing these "key" groups. Indeed, after the modification of the "key" groups, deeper aminoacid residues in the protein are usually involved, which as a rule destabilises it.[64,66] For this reason, if the "key" degree of modification of the protein has been missed in the experiment accidentally, then a stabilisation effect cannot be observed at all. Furthermore, for each specific protein and each new type of functional groups (for example, COOH, NH_2, SH, etc.), the empirical search for "key" groups must be carried out anew.

3. One may attempt to introduce into the protein molecule polar or charged groups by its modification, hoping that they will form new salt bridges with the functional groups already

present in the protein. Unfortunately, it is not easy to apply this approach in practice. For this purpose, it would be necessary to obtain maps of the steric structure of proteins and to search on the latter the uncompensated polar and charged groups which might, in principle, form new hydrogen bonds and enter into electrostatic interactions. Next, it would be necessary to find in the protein a suitable "anchor" group located in the vicinity of the uncompensated polar and charged group. Having selected or synthesised a suitable chemical agent, which would contain, on the one hand, a group reacting specifically with the anchor group and, on the other, a charged or polar fragment located at the specified distance, one could attempt to achieve the specific modification. It is not easy to perform such a delicate experiment.

4. According to some investigators,[223] the stability of proteins can be increased by rendering them hydrophobic. However, the experimental data concerning the influence of hydrophobic modification on the stability of proteins are contradictory. Together with stabilisation effects,[223] cases are known where the stability of proteins rendered hydrophobic is significantly lower than that of the native proteins.[225-227] This apparent contradiction can be explained as follows. If the hydrophobic residue (for example, the CH_3 group) is introduced on the surface of the protein, the latter should be destabilised. Indeed, as a result of the modification, the protein acquires a new thermodynamically unfavourable contact between the hydrophobic CH_3 group and water. However, there are exceptions to this general rule. As mentioned above, together with polar and charged aminoacids, there are on the surface of proteins also hydrophobic aminoacids which are frequently organised into hydrophobic surface clusters.[228,229] If the functional group located near such a cluster has been modified, then the modifying agent of suitable length cuts off the contact between the solvent and the cluster. One can imagine the situation where the interaction of the modifying agent with the cluster does not alter or even diminishes the area of the unfavourable contact between the hydrophobic surface of the protein and water. In any case, however, the modification results in the appearance of an additional contact between two hydrophobic surfaces, which should increase the stability of the protein.[223]

This view is also supported by the observed increase of the stability of certain proteins[230,231] as a result of complex formation with non-polar molecules (benzene and aliphatic acids). The interaction of proteins with these compounds can be represented in the way already described above. However, since this is a relatively weak non-covalent interaction, the protein–ligand complex dissociates readily when the excess of the non-polar substance is removed from the system. The formation of such non-covalent complexes can therefore hardly serve as the basis of a general method for the stabilisation of enzymes.

The modification permitting the introduction of a non-polar molecule into the interior of the hydrophobic core of the protein should be especially effective from the standpoint of stabilisation.[19] The essential feature of the approach permitting the attainment of this situation is that the initial state for modification is not the coiled (native) conformation of the protein but the uncoiled state (statistical coil). This state can be arrived at by treating the protein with a strong denaturant (urea) with the simultaneous cleavage of the S–S bonds[232] (in those proteins where these are present). An attempt may be made to alter the structure of the uncoiled protein in one of the three ways proposed. Firstly, it can be coiled up under "non-native" conditions, i.e. conditions which are not characteristic of the coiling process *in vivo*. There is hope that the protein will coil up into another conformation, which is also catalytically active but more stable. In particular, if the coiling is carried out under conditions favouring the enhancement of the hydrophobic contacts (concentrated solutions of salts, elevated temperature, etc.) then it is possible to obtain a protein conformation in which non-polar aminoacids are more "correctly" packed (the interior of the protein becomes more hydrophobic and the surface more polar). Secondly, it is possible to coil up the proteins in the presence of substances which enter into multipoint non-covalent interactions with them. Here non-polar and biphilic compounds are most promising in our view. The former can be captured in the interior of the hydrophobic core on coiling up the protein and the latter can be "built" into the coiled protein, being in contact via their non-polar fragment with the hydrophobic regions in the protein, while the polar or charged fragments are exposed to the solvent. Thirdly, the uncoiled protein can be modified initially by a chemical agent and then coiled up.

At the present time the approach described above is being actively developed.[233] We shall deal with only one experimental result. Immobilised trypsin was converted into the uncoiled state and then coiled up at different temperatures. The trypsin coiled up at 50 °C and above proved to be[19] more thermally stable than the initial enzyme or enzyme which had been coiled up at the usual (20–35 °C) temperatures. These results agree with data obtained *in vivo* for thermophilic microorganisms.[46,47,234-236] These organisms synthesise two sets of enzymes: stable and labile, and at high temperatures the content of the stable forms is significantly higher. The "high temperature" and "low-temperature" proteins are apparently the iso-forms of the same enzymes, having identical primary structures.[46,47] Consequently, as in model experiments, the protein *in vivo* also coils up into a more or less stable conformation depending on the temperature of the biosynthesis.

5. Finally, we shall consider the approach to the stabilisation of enzymes which we recently proposed[19] and which is being successfully developed at the present time.[237,238] It is based on the hypothesis that contact between the hydrophobic sections of the surface of the protein and water is thermodynamically unfavourable and therefore destabilises the protein. The idea of the approach is that the area of contact between the hydrophobic clusters on the protein surface and water be reduced by chemical modification.

Before applying this approach, it is essential to select a criterion of the hydrophobic character of chemical compounds. Hitherto, in discussing the influence of chemical modification on the stability of proteins, sufficient attention was not paid to this question; (see, for example, the relevant reviews[64-66]). The conclusion whether or not chemical modification of the protein rendered it hydrophobic or hydrophilic is sometimes self-evident and does not require accurate quantitative estimates. As an example of the evident acquisition of hydrophobic properties, one may quote the modification of α-chymotrypsin by aliphatic aldehydes.[224] Indeed, in this case, after the reduction of the Schiff base formed, the aminoacid groups of the enzyme are transformed into $-NH-(CH_2)_n-CH_3$. However, it is then hardly possible to estimate even qualitatively from general considerations how the hydrophilic character of the amino-group changes when it is modified by succinic anhydride [when the NH_2 group is transformed into $-NH-CO_2-(CH_2)_2-COOH$]. Nevertheless, such modification is frequently regarded as imparting hydrophilic properties.

We selected as the quantitative criterion of hydrophobic character the partition coefficient P of the compound considered between water and an immiscible organic phase proposed by Hansch and co-workers.[239,240] According to this criterion, the more positive the value of P, i.e. the greater the preference for the organic phase by the substance compared with the aqueous phase, the more hydrophobic it is. On the basis of the principle of the additivity of free energies,[241] it is possible to calculate the hydrophobic characters of various functional groups and atoms. For example, the hydrophobic increment per Cl atom (π_{Cl}) can be calculated from the experimental partition coefficient of two compounds: chlorobenzene and benzene:

$$\pi_{Cl} = \log c_{C_6H_5Cl} - \log c_{C_6H_6} = 2.84 - 2.13 = 0.71 .$$

Using this procedure, we calculated[239,240] the hydrophobic increments for the functional groups and atoms most frequently encountered in biochemistry (more than 150). Some of the values of π are listed in Table 7. The converse problem can be solved by this procedure in its turn—the hydrophobic characters of complex compounds can be estimated.

We suggest the application of the approach described above[239,240] for the estimation of the contribution by the chemical agent (modifying agent) to the change in the hydrophobic character of the protein. Quantitative analysis of this aspect permits a fresh view on certain experimental data concerning the chemical modification of proteins. Thus the oxidation of the Met-192 residue in α-chymotrypsin to the more hydrophilic form $S(O)CH_3$ increases the conformational stability of the protein by 2.1 kcal mol^{-1}. On the other hand, the difference between the free energy increments for the extraction of these groups from water into an organic solvent, namely $2.3RT(\pi_{SOCH_3} - \pi_{SCH_3})$, is very similar, i.e. 2.5 kcal mol^{-1} [240] (p.52). On this basis, one may postulate that the stabilisation of chymotrypsin observed following the oxidation of only one Met residue,[242] is caused precisely by the acquisition of hydrophilic properties by the surface of the hydrophobic cluster in the protein.

Another example of acquisition of hydrophilic properties is provided by the modification of the amino-groups of the protein (for example, by O-methylisourea) with their conversion into arginine-like structures. Table 6 shows that Arg is more hydrophilic than Lys. The numerous examples[243-248] of the stabilisation of proteins following the introduction of guanidino-groups into Lys residues can therefore be explained by the decrease of the area of contact between the hydrophobic protein and water.

A major stabilisation effect was achieved by aminating the tyrosine residues in trypsin.[237] The four tyrosine residues in the molecule of this enzyme are distributed on the surface.[249] The appearance of the amino-group in the aromatic ring of tyrosine increases its hydrophilic character by 1.24 kcal mol^{-1}. As a result of such increase in hydrophilic character, the stability in relation to irreversible denaturation of trypsin in which two and more tyrosyl residues have been modified increased by a factor greater than 100.[237]

The stabilisation method designed to render the surface of the hydrophobic clusters in the protein hydrophilic[19] has achieved the greatest successes in the acylation of α-chymotrypsin by the dianhydride of pyromellitic acid.[238] It was shown that the modification involves mainly the protein amino-groups and that three new carboxy-groups are introduced into the enzyme molecule on modification of each group. Thus, the preparation with the maximum degree of modification has been enriched by at least 50 COOH groups.[238] At weakly alkaline pH (thermal inactivation conditions), all the carboxy-groups are deprotonated and a very significant hydrophilic character of the protein surface has therefore been attained (Table 7). The modified enzyme is so much more stable than the native enzyme that it is impossible to select experimentally the temperature at which the kinetics of the inactivation of these two preparations can be compared. In order to estimate nevertheless the difference between their stabilities, it was necessary to extrapolate the experimental data (Fig.7) to an average temperature. For example, at 60 °C the stabilisation effect corresponds to a factor greater than 10^3, becoming still greater with increase of temperature, as can be seen from Fig.7.

Table 7. Parameters of the hydrophobic character of certain chemical groups.[240]

Group	π_{Ar}^{*}	π_{Alk}^{**}	Group	π_{Ar}	π_{Alk}	Group	π_{Ar}	π_{Alk}
H	0	0.23	OH	−0.67	−1.64	COOH	−0.32	−1.11
CH_3	0.56	0.77	SH	0.39	−0.23	COO^-	−4.36	−5.19
C_2H_5	1.02	1.43	OCH_3	−0.02	−1.54	$COCH_3$	−0.55	−1.13
$CH(CH_3)_2$	1.53	1.84	$NHCH_3$	−0.47	−1.38	CO_2CH_3	−0.01	−0.72
C_3H_7	1.55	1.97	CN	−0.57	−1.27	C_2H_4COOH	−0.29	—
C_6H_{11}	2.51	—	NO_2	−0.28	−1.16	$N(CH_3)_2$	0.18	−0.64
C_6H_5	1.96	1.90	NH_2	−1,23	−1.54	$\overset{+}{N}(CH_3)_3$	−5.96	—

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*The value of π for a substituent in the aromatic ring.

**The value of π for a substituent in an aliphatic compound.

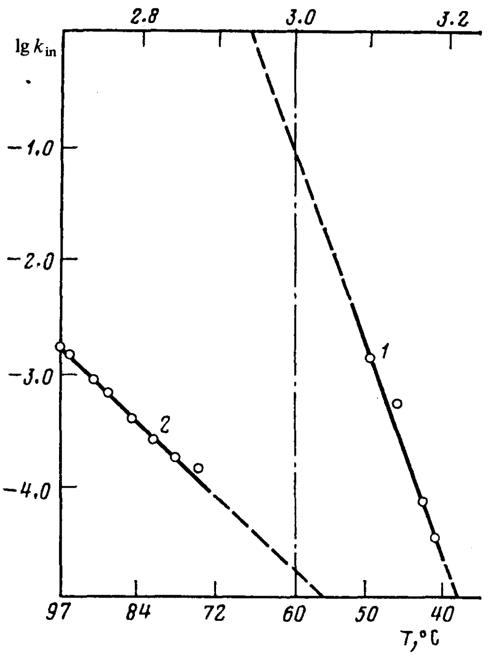

Figure 7. Temperature variation of the rate constant k_{in} for the thermal inactivation of native α-chymotrypsin (line 1) and α-chymotrypsin modified with pyromellitic dianhydride (line 2); the degree of modification of the acylated preparation is a maximum.[238]

Thus, by imparting hydrophilic properties to the surface of chymotrypsin (by introducing a large number of carboxylate anions), it is possible to attain[238] enormous stabilisation effects. Previously effects of this order were observed only on multipoint binding of the enzyme to the surface of a carrier[130,217,218] (see also the relevant reviews[11-19]). Thousandfold (and greater) stabilisation effects[238] are so far the highest achieved using low-molecular-weight modifying agents for proteins. The stability of the chymotrypsin modified by pyromellitic dianhydride is not inferior to that of proteases from extreme thermophiles[250] and is at present the most stable among all the known proteolytic enzymes.

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In the present review we attempted to anser two questions. Firstly, how to discover the structural determinants of the stability of proteins (i.e. the structural features and intra- and inter-molecular interactions which ensure an increased stability of the protein) and, secondly, which approaches and methodological procedures must be used in order to obtain, knowing these structural determinants of the stability of proteins, stabilised enzyme preparations for biotechnology. We do not share the pessimism which is frequently expressed concerning the possibility of recognising the molecular causes of the stability of proteins and of applying them in practice in order to devise stabilisation approaches. On the contrary, the advances achieved hitherto are extremely hopeful. We are confident that new methods and ideas (some of these were discussed or proposed in the present review) will generate an additional stimulus to studies in this field.

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Development of the Physical Chemistry of the Solvated Electron

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The principal results of experimental and theoretical studies of excess electrons in condensed media are examined and the physical nature of localised (solvated) electrons as well as the characteristics of the chemical and electrochemical reactions in which they participate are discussed.
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I. INTRODUCTION

In 1808 Davy observed the phenomenon involving the acquisition of a bronze colour by potassium in liquid ammonia,[1] which was evidently the first description of the effects associated with the formation of the solvated electron. Approximately 50 years later, a similar observation was made by Weyl,[2] who is traditionally regarded as the first investigator of the unusual physicochemical properties of metal–ammonia solutions. After Weyl's investigations, the interest in metal–ammonia solutions continued without interruption, passing through periods of growth and decline. It was shown that the unusual metal-like properties of metal–ammonia solutions are caused[3,4] by the "abstraction" of an electron from the metal. During the last decades it has been established that the states of thermalised excess electrons, whose nature is analogous, arise in many disordered condensed media, without intrinsic conductivity, under the influence of radiation or the injection (emission) of electrons.

The phenomena occurring following the introduction of excess electrons into the media indicated have become the subject of continued attention from investigators working in a number of branches of the physics of condensed media, chemical physics, radiation chemistry, and even biology. Since 1964, international conferences, called the Weyl Colloquia, have been held regularly on this topic. The proceedings of these conferences, containing important information about the state of research into the properties of excess electrons in condensed media, have been published.[5–10] The results of such studies are also presented in books and reviews whose authors have concentrated their attention on the physicochemical,[11–16] physical,[17–21] chemicophysical, and radiation-chemical[22–28] aspects of the problem.

Initially, mainly localised electronic states in polar liquids attracted the attention of investigators. Such electrons were called solvated and were designated by the symbol e_s. The interest in solvated electrons increased especially after the discovery at the beginning of the 1960's of the short-lived solvated (hydrated) electron e_{aq} in water and aqueous electrolyte solutions.[29] The very important role of e_{aq} in radiation-chemical transformations and in the alteration of the physical properties of irradiated aqueous systems was then established.[23–26] There exist a number of hypotheses concerning the possible involvement of e_{aq} in various biochemical reactions[30–34] and in the synthesis of organic substances accompanying the binding of nitrogen and involved in the origin of life on Earth.[26]

States analogous to e_s in polar liquids and differing sharply from the excited states of electrons in crystals have been discovered and investigated also in non-polar liquids—liquid inert gases and hydrocarbons.[19,22,35–39] The electrons captured in vitreous matrices at low temperatures have properties similar to those of e_s.[40] The extensive experimental data obtained proved in many instances to be unexpected and did not fit the existing theoretical schemes. Together with e_s, the so called "dry" excess electrons, resembling the delocalised conductivity electrons in metals, were discovered and investigated.† Bielectrons $(e_s)_2$—systems with a double charge exhibiting a specific reactivity—

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† Historically the term solvated electrons was given to localised equilibrium states of excess electrons in polar media. The term "dry" electrons is usually understood as the delocalised states of excess electrons, which have not as yet attained equilibrium with the "slow subsystem"—the polar medium. We may note that delocalised equilibrium states of excess electrons are also possible (if one leaves aside the consideration of chemical reactions involving excess electrons), which are called quasi-free electrons. Furthermore, the term "captured electron" (in the English language literature "trapped" electrons) is frequently encountered in the literature—this represents a non-equilibrium (quasi-equilibrium) localised state of the electron in frozen polar media (glasses). If one also takes into account the fact that excess electrons can exist in different excited states, the terminological difficulties of the authors become understandable. In subsequent exposition, the term "solvated electron" (e_s) should be understood in its initial (historically) sense, unless it is specially stipulated which particular quantum-mechanical state of the excess electron is being considered. We may point out that the questions of terminology have been considered in fair detail by Pikaev;[23,28] we shall be forced to return to them again in the Section devoted to the consideration of the energetic characteristics of excess electrons.

have also been discovered.[41] The synthesis of the latter aroused special interest among investigators in connection with the hypothetical possibility of constructing superconductors of a new type on the basis of their Bose condensate properties.[42,43]

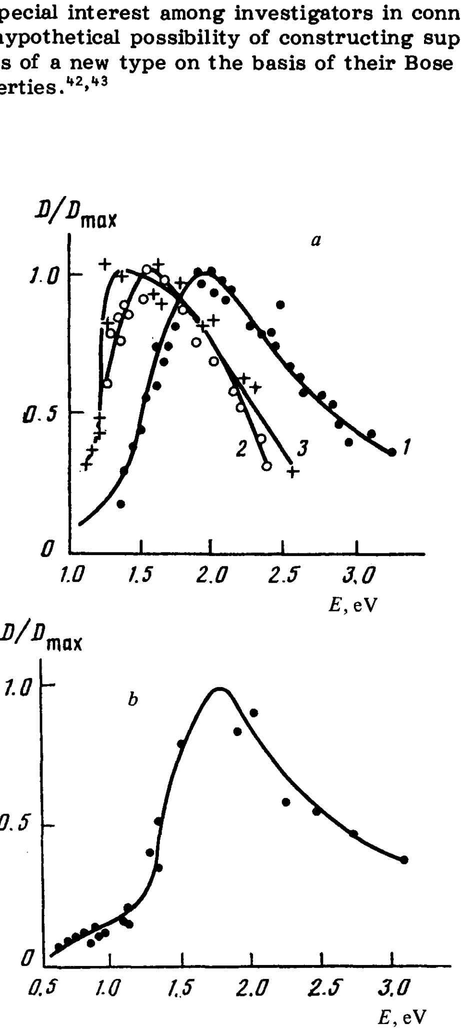

Figure 1. The absorption spectra of e_s in methanol at different temperatures (°C): *a*: *1*) 20; *2*) 148; *3*) 208; *b*: 244.[44]

The optical absorption curves for solvated electrons in different substances, their mixtures, and solutions, which have many properties in common, have been investigated in detail. In most cases these curves consist of a single broad structureless peak located in the visible or in the near ultraviolet depending on the microscopic structure of the solvent. The characteristic universal features of the shape of the absorption curves, to which we shall frequently refer below, are presented in Fig.1. Evidently the absorption peak is asymmetric: with increase of the energy, the comparatively sharp increase of the absorption is replaced by a slower descent. Such asymmetry is unusual in atomic and molecular spectroscopy (if one disregards the absorption spectra of a number of negative ions), but has analogies in nuclear physics.[21] In particular, the shape of the peak resembles very closely, after the appropriate alteration of the energy scale, the frequency dependence of the photosplitting of the deuteron. It was found that the shape of this absorption peak is extremely stable; for example, in the case of water it is almost invariant at temperatures from −4 °C up to a supercritical temperature. An important characteristic feature of the behaviour of the absorption peak from the standpoint of theory is its tendency to undergo a bathochromic shift with increase of temperature. It is seen in Fig.1 that the spectra of e_s in alcohol have the same features.

After a brief description of the various methods for the detection and investigation of e_s, we shall consider in the present review its physical nature, its chemical reactions, and its electrochemical behaviour. Special attention is devoted to the unusual nature of the chemical reactions of the solvated electron, the most active reductant, which is caused to a large extent by the possible occurrence of tunnel processes involving e_s. The characteristics of the thermodynamics of the solvated electron, including the thermodynamic relations between e_s and the quasi-stable "dry" electrons, will also be discussed.

II. EXPERIMENTAL RESEARCH METHODS

It is difficult to name an experimental physicochemical method which has not been used in the study of excess electrons in condensed media. This can be naturally accounted for by the fact that solvated electrons constitute unique experimental objects—the simplest anions which interact strongly with the medium and are characterised by both specific EPR and optical absorption spectra, readily generated by various procedures (pulsed and steady), having a wide variety of chemical properties, and, as already mentioned above, participating in many physicochemical processes. Therefore, regardless of whether the investigator is interested in quantum chemistry, magneto-resonance analytical methods, conductivity, the optics of condensed media, the chemistry of solutions, radiation chemistry, electrochemistry, cooperative phenomena, or other questions, the analysis of the nature and behaviour of excess electrons in various media enables him to test the selected method, to obtain interesting information, and to assess critically the existing theoretical schemes.

The possibility of using well tested physical methods, with a high time resolution, is an appreciable advantage in the study of solvated electrons (including the kinetics of their reactions). Here we have in mind in the first place the optical spectroscopic and EPR methods and also the method of induced pulsed electrical conductivity developed recently (and various modifications and combinations of the methods indicated). Most information about e_s has been obtained by studying the optical absorption spectra by an extremely wide variety of methods. High speed spectrometry with time resolution down to several picoseconds[45–53] with e_s generated by pulse radiolysis[48,50–53] and flash photolysis[45–47,49] has been used in the study of kinetics of the solvation and chemical reactions of e_s. Stationary and nanosecond spectra of e_s generated in different ways have been investigated as a function of temperature,[44,54] pressure,[55] the state of aggregation of the matrix (glass, liquid, and crystal), etc. Attempts (albeit with negative results) to observe the luminescence of solvated electrons have been described.[45,56]

Apart from the optical spectra, the IR and UV spectra of solvent–excess electron systems have been investigated.[57–59] Combined electro-optical,[60] magneto-optical,[61] and ellipsometric[62,63] methods are extremely promising. Excess electrons have also been investigated in experiments on photoemission and thermoemission from a metal into a solution and from a solution into a vacuum.[64–66] Many experiments concerning the influence of photoannealing on e_s spectra have been performed.[45–53] At the present time, one may claim that the optical properties of e_s have been more fully investigated than those of other colour centres in condensed media, including the usual halide ions. At the same time, to this day there is no generally accepted theoretical scheme which would explain the characteristic optical properties of e_s.

Various pulsed and stationary NMR and EPR methods have been used to investigate the immediate environment of solvated electrons.[7-12,19] Particularly valuable results have been obtained for frozen systems by the spin-echo modulation method.[67-69] The spin-echo modulation method, developed specially[67] for the investigation of solvated ions, has already yielded extensive information about the solvation shells of various metal ions in frozen electrolytes. However, in the case of e_s the results obtained must be treated with greater caution, according to Golden and Tuttle,[70] because in their interpretation one usually employs effective constants for spin interactions, which, as a consequence of the comparatively broad distribution of the e_s electron density, always have values as if the electron were localised in a cavity even when in fact there is no increase in the distances between the molecules of the medium at the site of the localisation of the excess electron.

There exist examples of the employment of fairly rare methods, such as the annihilation of positrons,[10,14] mass-spectrometric analysis of charged clusters of the type $(H_2O)_n^-$ in vapours,[71] and measurement of ultrasonic absorption.[10,14] Some of the results obtained by these procedures do not fit in any way the familiar theoretical schemes, which, incidentally, may be attributed to the inadequate accuracy and reliability of the selected experimental method.

Clearly, even a brief description of the experimental methods employed and the results obtained would occupy too much space. For this reason, we confined ourselves above to mentioning only the principal and most thoroughly developed fields of experimental research. We shall only state that, by analysing the nature of e_s, it is possible to assess fairly reliably various experimental and theoretical approaches in various fields of chemical physics.

III. THEORETICAL DESCRIPTION

The problem of the selection of an adequate model for the description of the solvated electron—an excess localised electron in a disordered, usually polar, condensed medium—is complex and interesting. Any progress towards its solution appears important not only for specialists, directly concerned with the solvated electron, but also for the general theory of condensed media.

During the period from 1940 to 1946, Ogg[72] developed the first quantitative theory of the electron solvated in ammonia. It was postulated that a spherical cavity with a radius R is formed around the electron in ammonia and that the ammonia molecules at the boundary of the cavity create for the electron an effective spherical potential well with infinitely high walls. The energy of the electron is made up of the positive kinetic energy T_e, determined with the aid of the uncertainty principle from the formula $T_e = (2\pi\hbar)^2/2mR^2$, and the energy of the interaction with the polarisation field:

$$V=-\frac{e^2}{R}\left(1-\frac{1}{\varepsilon_0}\right) \tag{1}$$

where ε_0 is the dielectric constant of the medium and m and e are the mass and charge of the electron.

The equilibrium value of the radius R_{eq} corresponds to the condition for a minimum in the total energy of the system. Ogg compared the "pushing apart" of the molecules by the electron in the cavity with the observed increase in the specific volume of ammonia following the dissolution of alkali metals in it. On excitation with light, the electron leaves the cavity. The threshold frequency Ω of the light absorbed by the solvated electron is determined from the relation

$$\hbar\Omega=T_e+V \tag{2}$$

The frequencies Ω and the high value R_{eq} = 20 Å obtained by Ogg clearly conflict with experiment. The main cause of this discrepancy is, as has now become clear, the unduly high kinetic energy of the solvated electron in the model of the potential well with infinite walls, which provides a poor description of the states of e_s, which are in reality comparatively weakly bound. However, the idea itself of the formation of a "cavity" greatly stimulated further theoretical investigation of e_s. In essence, an analogous computational scheme (with, however, the minimisation not of the energy but of the free energy of the electron—medium system) has been used as the basis of the modern description of the localised states of excess electrons in inert gases.[17,35-39]

Davydov[73] was the first to use for the description of solvated electrons in ammonia the Landau–Pekar theory of large radius polarons, developed previously[74] for the description of electronic states in ionic crystals. Subsequently this approach was used by Deigen.[75] Within the framework of the Davydov–Deigen theory, which its authors put forward in opposition to Ogg's cavity theory, it has been possible to obtain the quantitative values of a whole series of characteristics of the electron in ammonia in agreement with experiment, and in the first place the position of the maximum of the optical absorption band, which was related to the Franck–Condon 1s – 2p transition. This theory has played an important role in the prediction of the existence of and the determination of the frequency range in the optical absorption of the short-lived hydrated electron e_{aq}. On its basis, many attempts have been made to refine the calculations of the energy parameters and other characteristics of the ground and excited states of solvated electrons (see, for example, Mazurenko and Mukhomorov[76]).

The computational scheme, in which longitudinal optical phonons appear as collective excitations, has been most frequently used in the solvated electron theory. The appearance of such collective excitation is associated with the movement of a system of dipoles, whose orientation changes after the introduction of a charge into the system. The direct use of the theory of the interaction of electrons with phonons is possible only in the case of weak interactions with the aid of the procedures of the perturbation theory. Another limiting case, that of the strong interaction, is of greatest interest for the theory of solvated electrons. A special approach, whose main element is the use of an analogue of the Hartree self-consistent field method frequently used in quantum chemistry, has been developed for this purpose.

One of the most logical and clearest schemes for the representation of the above approach is as follows.[77] The complete vector of the state of the system $|\Psi\rangle$ is expressed approximately in the form of the direct product of the vector of the state $|\phi\rangle$, which depends solely on the electronic parameters, and the vector of the state $|\chi\rangle$, which depends only on the characteristics of the phonon field:

$$|\Psi\rangle=|\varphi\rangle|\chi\rangle \tag{3}$$

The exact Hamiltonian of the system H, i.e.

$$H=H_0^{el}+H_0^{ph}+\sum_{\mathbf{q}}(Q_{\mathbf{q}}a_{\mathbf{q}}e^{i\mathbf{qr}}+Q_{\mathbf{q}}^{*}a_{\mathbf{q}}^{+}e^{-i\mathbf{qr}})$$

is then replaced by the approximate Hamiltonian $\tilde{H}$, which depends explicitly on the time t:

$$\tilde{H} = H_0^{el} + H_0^{ph} + \sum_{\mathbf{q}} [Q_{\mathbf{q}} a_{\mathbf{q}} \rho_{\mathbf{q}}(t) + Q_{\mathbf{q}}^* a_{\mathbf{q}}^+ \rho_{\mathbf{q}}^*(t)] + \\ + \sum_{\mathbf{q}} [Q_{\mathbf{q}} A_{\mathbf{q}}(t) e^{i\mathbf{qr}} + Q_{\mathbf{q}}^* A_{\mathbf{q}}^*(t) e^{-i\mathbf{qr}}] + F(t) \tag{4}$$

where the summation is carried out with respect to the wave vectors of the phonons $\mathbf{q}$, H_0^{el} and H_0^{ph} are the Hamiltonians of the non-interacting electron and phonons respectively, $Q_{\mathbf{q}}$ is the shape factor of the electron–phonon interaction,# $a_{\mathbf{q}}$ ($a_{\mathbf{q}}^+$) the operator of the annihilation (generation) of the phonon, $\rho_{\mathbf{q}}(t)$, $A_{\mathbf{q}}(t)$, and $F(t)$ are certain (non-operator) time functions, and the asterisk * implies the complex conjugate. It follows from the condition for the minimum deviation of $\tilde{H}$ from H, which is formulated as the requirement for a minimum in the functional $<\Psi|(\tilde{H} - H)^2|\Psi>$ for all the vectors of the state $|\Psi>$ of type (3) that the following equations must hold:

$$\begin{gathered} \rho_{\mathbf{q}}(t) = \int \varphi^*(\mathbf{r}, t) \cdot \varphi(\mathbf{r}, t) \cdot e^{i\mathbf{qr}} d^3r \\ \varphi(\mathbf{r}, t) = \langle \mathbf{r} | \varphi(t) \rangle \\ A_{\mathbf{q}}(t) = \langle \chi | a_{\mathbf{q}} | \chi \rangle \\ F(t) = -\sum_{\mathbf{q}} [Q_{\mathbf{q}} A_{\mathbf{q}}(t) \cdot \rho_{\mathbf{q}}(t) + Q_{\mathbf{q}}^* A_{\mathbf{q}}^*(t) \cdot \rho_{\mathbf{q}}^*(t)] \end{gathered} \tag{5}$$

When the ground state is considered, the c-number term $F(t)$, which is independent of the coordinates and momenta of the electron and phonons can be rejected in the Hamiltonian (4), because its retention leads only to a change in the phase of the wave function which is insignificant when stationary states are considered. From Eqns.(4) and (5), it is possible to obtain dynamic equations which can be conveniently formulated for the wave function $\phi(r, t)$ of the electrons in the Schrödinger representation and for the phonon operators $a_{\mathbf{q}}$ in the Heisenberg representation:

$$\begin{gathered} i\hbar \frac{\partial \varphi}{\partial t} = \left\{ H_0^{el} + \sum_{\mathbf{q}} [Q_{\mathbf{q}} A_{\mathbf{q}}(t) \cdot e^{i\mathbf{qr}} + Q_{\mathbf{q}}^* A_{\mathbf{q}}^*(t) e^{-i\mathbf{qr}}] \right\} \varphi \\ i\hbar \frac{\partial a_{\mathbf{q}}\ (s)}{\partial t} = [\tilde{H}, a_{\mathbf{q}}] = \hbar\omega_{\mathbf{q}} a_{\mathbf{q}} + Q_{\mathbf{q}}^* \rho_{\mathbf{q}}^*(t) \end{gathered} \tag{6}$$

where $\omega_{\mathbf{q}} = \omega$ for the optical phonons and $\omega_q = C_s q/\hbar$ for the acoustic phonons.

In Eqns.(6), the electronic (phonon) field depends on the phonon (electronic) field solely via the average values of the corresponding operators, analogously to what happens in the Hartree method. The second Eqn.(6) represents the equation for an oscillator in the presence of an external force. The basis set of the so called coherent states, which remain coherent in the course of the evolution of the system in time, i.e. each coherent state passes to another specific coherent state corresponding to it, is convenient in this case. By selecting, in terms of the Heisenberg representation considered, a coherent state with an eigenvalue $\alpha_{\mathbf{q}}$ of the operator $a_{\mathbf{q}}$ at time $t = -\infty$, we have

$$a_{\mathbf{q}}(t) | \alpha_{\mathbf{q}} \rangle = \alpha_{\mathbf{q}}(t) | \alpha_{\mathbf{q}} \rangle, \ | \alpha_{\mathbf{q}} \rangle = \sum_{n_{\mathbf{q}}=0}^{\infty} \frac{\alpha_{\mathbf{q}}^{n_{\mathbf{q}}}}{n_{\mathbf{q}}!} | n_{\mathbf{q}}(t) \rangle \cdot e^{-|\alpha_{\mathbf{q}}|^2/2} \tag{7}$$

where $|n_{\mathbf{q}}(t)>$ is a state with a specified number of phonons and a wave vector $\mathbf{q}$. Bearing in mind that phonons with different $\mathbf{q}$ are independent in terms of the given approximation, it is sufficient to consider, instead of the second operator equation (6), the usual differential equation for the average values of $a_{\mathbf{q}}$ in terms of coherent states which enter into the first Eqn.(6):

$$A_{\mathbf{q}}(t) \equiv \langle \alpha_{\mathbf{q}} | a_{\mathbf{q}} | \alpha_{\mathbf{q}} \rangle \tag{8}$$

Thus, the second Eqn.(6) is replaced by the equation for the classical field $A_{\mathbf{q}}(t)$. Its solution is

$$A_{\mathbf{q}}(t) = A_{\mathbf{q}}^0 \cdot e^{-i\omega t} - i\hbar^{-1} Q_{\mathbf{q}}^* \int_{-\infty}^{t} e^{i\omega(t'-t)} \rho_{\mathbf{q}}^*(t')\, dt' \tag{9}$$

In the majority of the calculations carried out hitherto, the following two additional assumptions have been used (explicitly or implicitly). Firstly, the first term on the right-hand side of Eqn.(9) is rejected, which can be interpreted as abandonment of allowance for the influence on e_s of the real free phonons arising in the medium even at equilibrium due to thermal excitation. Secondly, the adiabatic approximation, consisting in the replacement of $\rho_{\mathbf{q}}^*(t')$ in the integrand in Eqn.(9) by $\rho_{\mathbf{q}}^*$—the average for the electronic ground state considered along a finite trajectory—is applied. The validity of the latter approximation is justified by the different time scales of the movements of the inertial phonon and rapid electronic subsystems.

After the replacement of the summation by integration, the problem of finding the stationary electronic function is reduced, in accordance with the usual rule, to its solution for the eigenvalues for a non-linear integro-differential operator:

$$E^e \varphi(\mathbf{r}) = [H_0^{el} - V_{sc}(\mathbf{r}, \varphi(\mathbf{r}))] \varphi(\mathbf{r}) \tag{10}$$

where

$$\begin{gathered} V_{sc}(\mathbf{r}, \varphi(\mathbf{r})) = \int d^3r' [|\varphi(\mathbf{r}')|^2 z(\mathbf{r}, \mathbf{r}')] \\ z(\mathbf{r}, \mathbf{r}') = \frac{1}{8\pi^3} \int d^3q \left\{ \frac{|Q_{\mathbf{q}}|^2}{\hbar\omega_{\mathbf{q}}} \cos[\mathbf{q}(\mathbf{r} - \mathbf{r}')] \right\} \end{gathered}$$

After solving the problem formulated above for the eigenvalues, the overall energy of the system can be represented in the form

$$E = E^e + E^m \tag{11}$$

where E^m is the energy of reorganisation:

$$E^m = \left\langle \alpha \middle| \sum_{\mathbf{q}} \hbar\omega a_{\mathbf{q}}^+ a_{\mathbf{q}} \middle| \alpha \right\rangle = \sum_{\mathbf{q}} \frac{|Q_{\mathbf{q}}|^2 \cdot |\rho_{\mathbf{q}}|^2}{\hbar\omega} = \\ = \frac{1}{2} \iint d^3r\, d^3r' [|\varphi(\mathbf{r}) \cdot \varphi(\mathbf{r}')|^2 z(\mathbf{r}, \mathbf{r}')] = \frac{1}{2} d^3r \varphi^*(\mathbf{r}) V_{sc} \varphi(\mathbf{r}) \tag{12}$$

In calculating E^m, Eqn.(9) was used for $A_{\mathbf{q}}$ without taking into account the free phonons.

The direct solution of Eqn.(10) with substitution in it of a particular specific expression for $z(\mathbf{r}, \mathbf{r}')$ represents an extremely complex problem, which is usually solved by variational methods.

#In the "classical" theory of the polaron, the shape factor $Q_{\mathbf{q}}$ assumes the form $Q_{\mathbf{q}} = -i(\pi\alpha_F/V)^{1/2} (\hbar^5\omega^3/m)^{1/4} q^{-1}$, where $\alpha_F = (\varepsilon_\infty^{-1} - \varepsilon_0^{-1}) (e^2/\hbar\omega)(m\omega/\hbar)^{1/2}$ is a dimensionless coupling constant (Fröhlich constant), ω and $\mathbf{q}$ are the frequency and the wave vector of the optical phonon, ε_∞ and ε_0 are the high-frequency and static dielectric constants of the medium, and V is the volume of the system. If interactions with acoustic phonons are considered, then $\omega = \omega(q) = C_s q/\hbar$ and $Q_{\mathbf{q}} = -i\sigma(\hbar q/2MC_sV)^{1/2}$, where C_s is the velocity of sound, M the mass of the unit cell, and σ the constant of the deformation potential.

The question of the limits of applicability of the numerous approximations introduced in the description of the strong coupling of electrons with phonons set out above is fairly complex. In the first place it is known that the Hartree type self-consistent field approximation cannot be characterised as an expansion in terms of a small dimensionless parameter and is justified in definite specific cases only as a result of certain numerical cancellations. One can only claim that such approximation is known to be applicable to a large number of phonons or, what amounts to the same thing, at high temperatures T in the system considered, because the correct classical limit for phonon equations is then obtained in terms of the basis set of coherent states. The additional adiabatic approximation used is known to be unjustified in the description of excited electronic states in the vicinity of the boundary of the continuous spectrum. The question of the methods of calculation of excited states with the aid of the variational procedure considered remains in general open. Its logical realisation requires expressions for the wave functions of higher states, which are so far unknown. Indirect estimates of the difference between the energies of the excited and ground states, which are in principle feasible, are extremely inaccurate. Referring to adiabatic conditions, the excited states in optical transitions are frequently calculated using the Hamiltonian of the ground state. This approach is quite justifiably disputed by Devreese et al.[78]

To the considerations presented in the studies quoted above, one must add that, when optical transitions are considered, one cannot simply reject, which is frequently done, the time(t)-dependent c-number terms $F(t)$ in Eqn.(4), such terms being different in different states. The fact that the theory must take into account quantitatively the effects arising owing to the disorder in the medium is significant. Logical allowance for these effects and also for microscopic interactions, symbolically introduced into Eqn.(4), within the framework of polaron models remains so far a matter for the future.

In connection with the uncertainty of the initial postulates of the theory, comparison of the conclusions which follow from it with experimental data is especially important. As already stated, many attempts have been made at a direct application of the large-radius polaron theory, in which the interaction with longitudinal optical phonons is specified by the Fröhlich Hamiltonian and there are no microscopic interactions, to the description of solvated electrons (see Refs.73–76 and the references in the last paper). However, this theory proved to be unable to explain many properties of solvated electrons. It has not been possible to interpret with its aid the shape of the optical absorption curve, the temperature dependence of the position of the maximum on this curve, and the influence of the phase state and pressure of the medium.§

The fundamental questions concerning the mechanism of the solvation of the electron have been investigated experimentally in a series of studies.[80–82] The authors investigated the optical spectra of e_s in mixtures of associated polar liquids having different or similar dielectric constants and also the changes in the spectra of e_s following the dilution of polar liquids by a non-polar solvent which is neutral as regards association. The most important result is the conclusion that the properties of e_s are correlated with the microstructure of the mixtures and that there is no dependence of the spectroscopic characteristics of e_s on the macroscopic parameters of the system (dielectric constant, density, etc.). On the basis of their experimental data, the authors[80–82] claim that the intrinsic structural elements of the medium—hydrogen bonded complexes of different molecules or self-associated species which function as electron traps—are of decisive importance for the mechanism of the solvation of the electron. The main cause of the broadening of the spectrum is the distribution of e_s among different associated species.[82]

Subsequently the approach proposed[80–82] was extended to dilute solutions of ammonia in various alkanes. The optical absorption corresponding to the photoexcitation of electrons localised in the associated polar molecules was then observed and investigated. The very fact of the solvation of the electron at very low concentrations of the polar component in the mixture (approximately 0.1 mole %) is of interest. The spectrum of e_s then remains almost the same as in pure NH_3 even when the medium is non-polar. The solvated electrons in such systems can probably be regarded as analogous to excess electrons in the vapours of polar liquids[83] and the spectrum of e_s then makes it possible to infer the energy characteristics of the electron in an "isolated" cluster of polar molecules.

The need to take into account in the solvated electron theory the influence of specific chemical interactions of e_s with the medium, which follows from the analysis of the experimental data, led to the development of semicontinuous models. Apart from the long-range interactions of e_s with long wavelength phonons, in such models account is taken, mainly phenomenologically, of the interactions with the molecules in the immediate environment—the solvation shell. Analysis of such models and of the difficulties associated with their use in the interpretation of experimental data, in the first place of the absorption spectra of e_s, has been carried out.[22]

The difficulties arising when the interactions of the electron with the solvent as a continuous system are considered stimulated the development of alternative theoretical models based on microscopic interactions of e_s with clusters—a small number of molecules surrounding the electron. These clusters are investigated by quantum-chemical methods. Such calculations for e_s are sometimes referred to as *ab initio* calculations for the electron. Using the terminology of solid state physics, the cluster models are seen to be closest to small radius polaron models. By virtue of the characteristics of a disordered medium, a tunnel electron jump is in this case difficult, because the equivalent position may prove to be fairly remote. If the characteristic time of any kind of processes involving e_s, for example optical transitions, is shorter than the characteristic time of the jumps, then the latter can be altogether neglected in the study of the given processes, i.e. the electron may be regarded as fixed at a specific molecular cluster.

In one of the first studies on these lines,[84] the states of the excess electrons in systems comprising water and ammoni dimers for a specific fixed geometry of the molecules in the dimers were calculated within the framework of a simplified version of the molecular orbital theory. For excitation energies identified with the difference between the energies of the lowest and highest orbitals, $\hbar\Omega = 2.5$ eV in the case o H_2O and 1.63 eV in the case of NH_3 were obtained.

The first quantum-chemical calculations for e_s revealed also the main difficulties encountered. It was found that (1) the state of e_s in the dimeric model is relatively unstable as regards the escape of the electron to a quasi-free state

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§ The question of the influence of temperature and pressure on optical spectra has not been finally solved even for the classical case of large radius polarons.[79]

and (2) the electron (especially in an excited state) is not localised within the limits of the cluster. In order to eliminate these difficulties, clusters consisting of a large number of molecules were considered in subsequent studies and also attempts were made to take into account the influence of the dielectric continuum outside the solvation sphere (cluster). Such *ab initio* calculations for clusters consisting of four water or ammonia molecules have been carried out.[85,86] They yielded not only extensive numerical information, in general in agreement with experimental data (we have in mind the optical transition energies $\hbar\Omega$ and the geometrical dimensions of the clusters), but also involved a discussion of the question of the stability of the states of e_s. It was found that the overall energy E_s represents the difference between two quantities: the energy gain in the localisation (capture) of the electron in the cluster with the optimum configuration and the energy expenditure necessary for the formation of such a cluster (or defect). The overall solvation energy E_s is positive although not large.[86]

However, in our view the energy gains obtained in the solvation of the electron are comparable to the accuracy of the calculation and the question of the stability of the clusters (i.e. of their existence in the vapour phase) should still be regarded as open. The above studies[85,86] have confirmed but not eliminated the difficulties arising in quantum-chemical models in view of the large effective radius of e_s in the excited state. In view of this result, the calculations of the characteristic excited states of e_s must be treated with a great deal of scepticism, because the interactions of the electron with the molecules of the second solvation shell should be significant for such states.

An evident deficiency of the above studies is their complete neglect of the interactions of the electron with the medium surrounding the cluster. Such interactions should lead to at least two effects; firstly, owing to the influence of the medium, the discrete lines in the absorption spectra of the cluster e_s should spread (or the corresponding vibronic bands should be modified); secondly, the presence of the medium can lead to an increased stability of the localised e_s (for example, via the polaron mechanism).

A configurational model of e_{aq} has been proposed.[87] The states of the H_2O^- ion, in the field of six dipoles interacting with one another which consist of the molecules in the first solvation shell, have been calculated by the LCAO method. The local energy minima of the cluster, corresponding to the electronic ground state of e_s, have been calculated as a function of the orientation of the dipoles. The "Franck–Condon" excited states of e_s were then found for each such local minimum in the energy of the cluster. The optical absorption spectral lines for such a cluster *in vacuo* should correspond to the differences between these energies. The attempt at a quantitative calculation of not only the main characteristics of the optical absorption band of e_s but also of the dependence of the spectrum on temperature and pressure must be regarded as a fundamentally new step in the study of Byakov et al.[87]

For the description of the absorption spectrum of the solvated electron, the above workers[87] resorted, apparently for the first time in quantum-chemical calculations of this kind, to the general theory of the absorption of light by impurity species in the medium. This general theory, developed by Ovchinnikov and Ovchinnikova,[88] relates the broadening of the discrete lines to the interaction of the electron with the optical phonons of the medium. Analysis of the spectrum of e_{aq} within the framework of the configurational model showed that, depending on the disposition (orientation) of the dipoles in the first solvation shell, there are several groups of stable "ground" states of e_{aq} (i.e. local energy minima of the electronic ground state). Its own "Franck–Condon" excited state corresponds to each of these ground states. It has been observed that the energies of the Franck–Condon transitions decrease on average with increase in the energy of the "ground" state. This finding explains the effect of the bathochromic temperature-induced shift of the absorption maximum: with increase in temperature, increasingly high "ground" states, which correspond to absorption in a longer-wavelength region, are populated. The interaction of the cluster with the medium leads to the spreading of the discrete spectral lines and to the appearance of a structureless spectral band, which is displaced to the left along the frequency axis if the temperature is increased. Since the band width is mainly related to the disposition of the initially discrete lines, its temperature dependence may not follow the proportionality to $\varepsilon_\infty^{-1} - \varepsilon_0^{-1}$ predicted by the polaron theory[76] and this also applies to the asymmetry of the band.

The experimental EPR data for e_s, indicating (in terms of the usual interpretation) the symmetry of the electron density distribution among the 4–6 protons of the immediate environment, may constitute an evident objection against the above model.[87] However, the authors[87] took into account this possible objection and carried out an analysis of the EPR spectra of e_s in terms of their model. An unexpected conclusion arising from this analysis is that of the possible equivalence of protons from the standpoint of EPR spectroscopy accompanied by a clear geometrical asymmetry of the disposition of the molecules in the configurational model (we recall that initial localisation of the electron in the cluster on one central H_2O molecule is postulated). The observed uncertainty in the reproduction of the geometrical structure of e_s on the basis of EPR data must be borne in mind also in the interpretation of complex spin echo experiments (see also Golden and Tuttle[70]). Unfortunately the authors[87] did not continue an analogous analysis of e_s for other media and it therefore remains unclear whether the mechanisms of the bathochromic shift, broadening, and asymmetry of the optical absorption band of e_{aq} which they quote[87] are universal for all (or the majority) of solvents or whether they apply only to H_2O.

The attempt to take into account the dielectric continuum has also been undertaken in a study[89] whose author reformulated the usual self-consistent field problem in terms of the Hartree potential and included the corresponding polaron contribution to the minimised energy functional in the quantum-chemical calculation for a negatively charged cluster consisting of four molecules of the medium. The calculation confirmed yet again the conclusion that the state of e_s in the gas phase is unstable, that the electron cloud incorporating the molecules of the medium adjoining the cluster has a large radius, and that the electron is almost fully delocalised in the excited state. Unfortunately, in the above study[89] the question of the shape of the absorption band and of its temperature dependence was not considered. The broadening of the band was explained qualitatively by the presence of geometrically different clusters, i.e., as is usual for cluster models, a heterogeneous mechanism for the broadening of the band was postulated.

It is noteworthy that a non-empirical calculation for a negatively charged cluster incorporating 4–6 molecules is at the limit of feasibility as regards modern computers and many natural questions, for example, concerning the infrared spectra of such clusters or the constants for the interaction of an additional electron with the intramolecular vibrations therefore still remain unanswered. It must be emphasised yet again that the quantum-mechanical methods used in the study of e_s provide only more or less approximate results and it would be naive to expect to obtain with their aid answers to all the questions. Experiments still remain the principal source of information.¶

The complex problems arising in the comparison of different theoretical computational schemes for e_s, the presence of a large number of parameters, and the uncertainty of the initial data led to studies in which the structure of e_s was investigated with the aid of methods of analysis of optical spectra unrelated or weakly related to model representations.[22,90–95] Such analysis indicates primarily the short-range character of the interactions leading to the localisation of e_s and makes it possible to treat optical absorption as electron transition from a bound state to a continuum.

We believe that the most convincing confirmation of the transition from the bound state to a continuum is provided by the results of the analysis of absorption spectra with the aid of optical sum rules, the virial theorem, and threshold formulae.[22,90–95] In an early study[96] it was already noted that the region of the characteristic absorption peak of the solvated electron corresponds virtually to the maximum value of the oscillator strength. Hence it was possible to conclude that at least the given peak corresponds to the transition of e_s to a continuum. Detailed analysis of the experimental results based on a wide variety of sum rules and model-free threshold formulae[22] demonstrates quite convincingly that the optical section of the absorption spectrum of the solvated electron does indeed correspond to the "bound state–continuum" transition. The long-energy sections of the spectrum can then correspond in certain specific cases to contributions by "bound state–resonance level" transitions. The contributions of such transitions are apparently extremely significant in the case of the electron in ammonia. The conclusions reached in a review[22] and in subsequent communications[92–95] concerning the analysis of the moments (optical) of the spectral absorption curves of the solvated electron are mainly in agreement. A significant feature of the above studies[92–95] was the discussion in the latter of the influence of the temperature of the system on the sum rules.

One of the most important conclusions from the model-free analysis of the optical absorption spectra of solvation electrons with the aid of sum rules and threshold formulae is that the interactions retaining the electron in the localised state are short-range in character.[22] A direct consequence of this conclusion has been an attempt to describe the optical spectra of the solvated electron within the framework of the stationary short-range potential model. The first study based on this approach was apparently that of Kajiwara et al.[97], in which the radial dependence of the potential was represented by a rectangular well characterised by two parameters. This approach has definite features in common with the cavity model adopted as early as the 1940's in Ogg's studies.

The studies summarised by Frankevich and Yakovlev[22] dealt with the so called zero radius potential with a single parameter expressed directly in terms of a quantity having a direct physical significance, namely in terms of the energy of the bound state of the electron. The zero radius potential, actively employed in nuclear physics, has the significance of the limit of the potential of the rectangular well (in terms of the zeroth spherical harmonic) when the width of the well tends to zero and its depth tends to infinity so that the single stationary level (or the antibonding state) does not change. Systems in a short-range potential field, the energy of the systems being close to the continuous spectrum threshold, are satisfactorily described in a similar way.

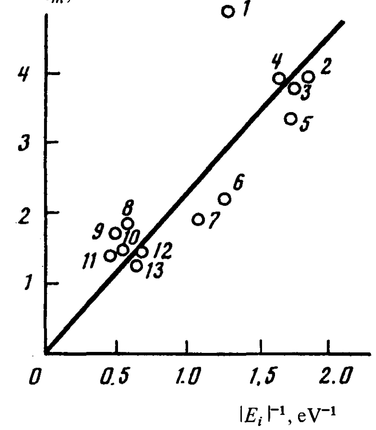

Figure 2. The extinction coefficient at the absorption maximum expressed as a function of $|E_i|^{-1}$. Straight line—theoretical relation corresponding to the zero radius potential model; circles—experimental data: *1*) ammonia; *2*) diethyl ether; *3*) methyltetrahydrofuran; *4*) tetrahydrofuran; *5*) dimethoxyethane; *6*) 1,3-propylenediamine; *7*) ethylenediamine; *8*) water; *9*) methanol; *10*) ethanol; *11*) ethylene glycol; *12*) isopropyl alcohol; *13*) 1-propanol.[44]

It is possible to extend the zero radius potential to the case of certain bound states, including states with the highest angular momenta, which is usual for specific systems with solvated electrons. The number of "adjustable" parameters can be increased by passing to potentials with a finite radius. In the case of the zero radius potential, the dependence of the cross-section σ of the photoinduced "bound state–continuum" transition on the frequency of the incident light Ω and on the energy of the initial state E_i is expressed by the simple formula

$$\sigma(\Omega, E_i) = \frac{32\pi^2 e^2}{3c\hbar} k_i \left(\frac{k_f}{k_f^2 + k_i^2}\right)^3 ,$$
$$\hbar^2 k_i^2 = 2m|E_i|; \ \hbar^2 k_f^2 = 2m(E_i + \hbar\Omega) . \qquad (13)$$

Eqn.(13) reproduces very satisfactorily in many instances the principal characteristics of the main absorption peak of the solvated electron. For example, according to Eqn.(13), there should be a linear relation, with a rigorously defined coefficient, between the extinction coefficient ε_m at the absorption maximum [which is proportion to $\sigma(\Omega_m)$] and the reciprocal of the frequency Ω_m^{-1}, corresponding to the absorption maximum. The corresponding theoretical curve together with the experimental points for a series of substances[90] is shown in Fig.2. The only deviation of the experimental points from the theoretical curve, exceeding the experimental

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¶In this connection one cannot fail to mention again the study[62] in which an ellipsometric investigation of e_s in hexamethylphosphoramide revealed a change in the vibration frequency of the non-polar C–H bond but no influence of the excess electrons on the polar C–N and P=O bonds was observed. This information necessitates in many respects a re-examination of the initial postulates for the construction of cluster models.

error, is observed in the case of the electron in ammonia. This finding is attributed[90] to the comparatively large interaction region (the presence of a "cavity") in the case of ammonia. Agreement with experiment can be attained if it is assumed that the size of this "cavity" in ammonia is in the range 1–2 Å. The relation between Ω_m and the threshold energy, which follows from Eqn.(13), also holds very satisfactorily:[22]

$$\hbar\Omega_m \cong 2|E_i| \ . \tag{14}$$

It is useful to quote the results of the analysis of the expression for the polarisability of the solvated electron α. In the general case of the motion of the localised electron with an energy E_i in an external potential field, the polarisability is given by

$$\alpha = K\frac{e^2\hbar^2}{mE_i^2} \ , \tag{15}$$

where K is a numerical multiplier. For the zero radius potential, the multiplier K assumes the minimum value $K = 1/16$ for the ground 1s state, while for a long-range potential of the Coulombic type, this quantity is 70 times greater and amounts to 9/2. For the remaining monotonic potentials, K lies in the range between 1/16 and 9/2. The polarisabilities obtained using the sum rule[22] for electrons in different media and the theoretical relation (15) for $K = 1/16$ are compared in Fig.3. The satisfactory agreement of the results constitutes important additional evidence in support of the short-range character of the interactions promoting the localisation of the electron in the solvated state.

However well the behaviour of the solvated electron is described with the aid of the zero radius potential model, such description is known beforehand to be incomplete, since it does not take into account the influence of many-particle effects. However, precisely these effects determine interesting phenomena such as the dependence of the shape and position of the absorption peak in the optical frequency range on the structure of the medium and temperature and also the manifestation of absorption in the infrared region associated with the modification of the collective modes as a result of the introduction of an excess electron into the medium. They also influence the kinetics of processes with participation of the solvated electron.

The question of allowance for many-particle effects in the solvated electron theory has been frequently posed in the literature. The problem has been most often considered in terms of a linear treatment based on the formulation of the Hamiltonian H taking into account the interaction and dynamics of the motion of all the particles in the system considered or, at least, sufficiently large clusters. One of the examples of this approach has been given by Golden and Tuttle.[98] In an approach of this kind, the introduction of insufficiently well-founded approximations and hypotheses of a model character is inevitable even when large computers are used for the calculations. Without denying the importance of such studies, we nevertheless doubt if real advances can be achieved on these lines, especially if an explanation can be found for the observed simple and universal characteristics of the behaviour of the spectra of solvated electrons.

We believe that another approach, corresponding to a scheme actively and successfully used in modern physics of condensed media is more promising. According to this scheme, the short-range interactions to which correspond the greatest changes in the energy of the system when a solvated electron is introduced into it are assumed to be specified and parametrised with the aid of a finite number of parameters, which can be calculated, in principle, by quantum-chemical methods. In the case of the solvated electron, the parameters of the zero radius or separable potential can be used as parameters of this kind. On the other hand, the long-range interactions are regarded as interactions with long-wavelength low-energy collective excitations of disordered media. Precisely such interactions determine, for example, the temperature effects for a constant density and also the principal kinetic features of the phenomena considered. The approach described has much in common with the semicontinuous model mentioned above, the only difference being that the interactions are separated in accordance with their energy and not spatial scale. An attempt to apply the above approach to the elucidation of the temperature dependence of the optical spectra was made in our earlier study.[99]

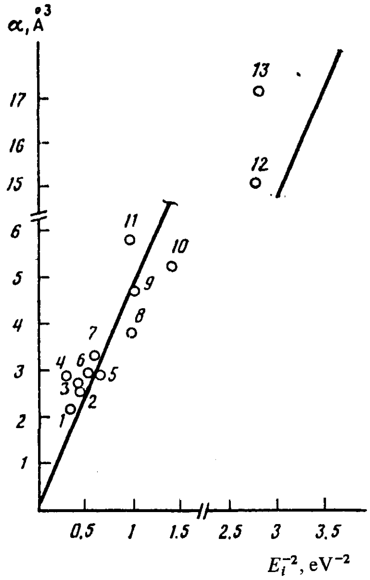

Figure 3. Dependence of the polarisability α on E_i^{-2}. The theoretical straight line corresponds to the zero radius potential model; circles—expermental data: *1*) methanol; *2*) 1-propanol; *3*) ethanol; *4*) 10 M KOH; *5*) diethylene glycol; *6*) 1-butanol; *7*) isobutyl alcohol; *8*) isopropyl alcohol; *9*) water (25 °C); *10*) 2-aminoethanol; *11*) water (–4 °C); *12*) *NN*-dimethylaminopropylamine; *13*) diethylenetriamine.[44]

IV. CHEMICAL REACTIONS

The chemical reactions of e_s in water, alcohols, ketones, and other polar liquids have been studied in especially great detail in the radiation chemistry of solvating compounds. The corresponding reactions have been described in a number of monographs[16,19–21,71] and we shall not deal with them in detail. In recent years much attention has been devoted to the detailed mechanism and other features of the reactions of e_s in mixtures of various solvents and to the reactions of stable e_s with a number of compounds dissolved in liquids such as ammonia, amines, and hexamethylphosphoramide.

We shall consider initially the bimolecular and unimolecular reactions of solvated electrons with water as the most important examples:

$$2\,e_{aq} + 2\,H_2O \rightleftarrows H_2 + 2\,OH^- , \qquad (16a)$$

$$e_{aq} + H_2O \rightleftarrows H + OH^- . \qquad (16b)$$

The analogous reactions in pure ammonia, i.e.

$$2e_s + 2NH_3 \rightleftarrows H_3 + 2NH_3^- \qquad (17a)$$

$$e_s + NH_3 \rightleftarrows H + NH_2^- , \qquad (17b)$$

hardly occur and e_s is extremely stable. The kinetic and thermodynamic characteristics of reactions (16) and (17) are presented below (at room temperature):

Reaction	k, litre mol^{-1} s^{-1}	ΔH^0, kJ mol^{-1}	ΔS^0, J mol^{-1} K^{-1}
(16a)	$5\cdot10^9$	−397	−12
(16b)	10^3	10	−48
(17a)	$\leqslant 1$	−168	−466
(17b)	$\leqslant 1$	125	−272

The kinetic data for the reactions were taken from Antropov[16] and the thermodynamic data from Schindewolf.[100]

Thus the absence of appreciable reactions of e_s in ammonia is caused by kinetic and not thermodynamic factors. The high absolute entropy of the solvated electron in ammonia $|S^0| = 169$ J mol^{-1} K^{-1} [101] (the entropy of the hydrated electron is $|S^0| = 13$ J mol^{-1} K^{-1}) leads to a high activation energy for the reactions of e_s in ammonia according to the activated complex (transition state) theory.[100–103]

The above arguments should also indicate a low probability of the reaction of the electron solvated in ammonia with admixtures of water ($\Delta H^0 = 52$ kJ mol^{-1}, $\Delta S^0 = -316$ J mol^{-1} K^{-1}):[103]

$$2e_s + 2H_2O \rightleftarrows H_2 + 2OH^- . \qquad (18)$$

The possibility of an endothermic unimolecular reaction is apparently ruled out in this instance. However, direct experiments have shown[104–106] that the electron in ammonia reacts with added water at an appreciable rate, which has not so far been unambiguously explained. It has been suggested[103] that the acceleration of this reaction is caused by the formation of an unknown intermediate X in accordance with the scheme

$$2e_s = (NH_3) + 2H_2O \rightarrow [2X] \rightarrow H_2 + 2OH^- . \qquad (19)$$

Evidence for the formation of intermediates in the reaction of e_s with water had been obtained earlier in experiments involving flash photolysis with additional lower-frequency illumination displaced in time relative to the initial pulse.[107,108] It was suggested that such intermediates may be the bielectron $(e_s)_2$, formed via the recombination of two solvated electrons, and, in a sodium–ammonia solution, the neutral complex (Na^+e_s), which is much larger than the Na atom. The question of the possible formation of $(e_s)_2$ and of complexes of the type $[Na(e_s)_2]$ has attracted much attention.[25] The detailed microscopic mechanism of even the most thoroughly investigated reactions of e_s with water cannot so far be regarded as unambiguously elucidated.

Much attention has been devoted recently to the reactions of e_s with aromatic and unsaturated hydrocarbons in various solvents and to reactions modelling processes involving charge transfer (electron capture by an acceptor). Studies of reactions with aromatic compounds[109–113] made it possible to identify the ranges of parameters within which the rates are controlled either by diffusional or kinetic limitations. In the case of diffusion-dependent control, the fact that the localised solvated electron e_s is in equilibrium with a delocalised "quasi-free" electron e_d assumes special importance. Although the fraction of delocalised electrons is small, their mobility is high and may determine the characteristic features of the migration. On the other hand, in most reactions (except perhaps the reactions of H atoms) the rate of interaction with e_s is much greater than the rate of interaction with e_d in conformity with the Franck–Condon principle. Thus, as noted for the first time by Frankevich and Yakovlev,[22] when the reactions of the solvated electron are considered account must be taken of both possible (localised and delocalised) states of the latter.

After the publication of the study of Frankevich and Yakovlev,[22] other communications appeared in which a system of two differential equations, corresponding to different states of the electron linked to one another by an equilibrium constant, is used instead of a single (diffusion) equation for the formal diffusional description of e_s capture and neutralisation processes.[18,114] The exact solution of such equations is difficult. The usual simplification is the hypothesis that the mobility (diffusion coefficient) of the electron in the localised state is much lower than the mobility (diffusion coefficient) of the quasi-free electron. On this hypothesis, it is possible to retain the form of the experimental relaxation curves and the values of the "adjustable" parameters become more reasonable.

This type of approach has been used in a study[114] whose authors began with generalised Noyes formula[115] for the effective reaction rate constant:

$$k_{\mathrm{eff}} = [pk_s + (1-p)\,k_d]\Big/\left[1 + \frac{pk_s + (1-p)\,k_d}{R_r D_{\mathrm{eff}}}\right] , \qquad (20)$$

where p is the probability of the localisation of the electron, k_s and k_d are the rate constants for the reactions with acceptors in the localised and delocalised states respectively, D_{eff} is the effective diffusion coefficient of the electron, and R_r is the reaction radius. In this way it has been possible, in particular, to explain the observed non-monotonic nature of the dependence of k_{eff} on the mobility of the solvated electron μ in the reactions of the latter in various hydrocarbons. Qualitatively, this phenomenon can be explained as follows. For low values of μ, the reaction proceeds under diffusion controlled conditions and the reaction rate constant is proportional to the mobility. The increase of the mobility promotes an increasing delocalisation of the electrons, which reduces the effective rate constant (subject to the condition that the reaction with the acceptor in the localised state is much faster than in the delocalised state). With the aid of the model considered, the authors[114] were able to explain also the dependence of the activation energy of the reaction on the effective mobility of the electron in hydrocarbons.

In the study of the kinetics proper of the reactions of solvated electrons with aromatic compounds, the validity of correlations involving a linear dependence of the rate on the free energy change in accordance with the Hammett equation was considered.[111] After the studies of Marcus[116] and Levich,[117] most attention was devoted (see Kestner[118] and the literature quoted therein) to the general theory of processes of the type

$$T^- + A \rightarrow T + A^- \qquad (21)$$

where T denotes a trap for the solvated electron ($e_s \equiv T^-$), which disappears over a finite period after it loses its charge.

One of the reasons for the interest in reaction (21) is that it is the simplest example of charge transfer. Furthermore, reactions (21) are included among the elementary steps of many electrochemical and biological processes. Processes involving e_s can be followed directly with the aid of effective optical methods with a short resolution time. Additional difficulties in the theoretical study of reactions (21) are associated with the need to allow for non-adiabatic effects. The most important qualitative result of the theoretical and experimental studies of the above reactions is the conclusion that electron transfer over a large distance is impossible and that this process is influenced by the orientation of the molecules of the medium, especially in biological systems and glasses.[119]

In conclusion of the present Section, we may point to the possibility, established recently (see the review of Glausinger et al.[42] and the literature quoted therein), of the formation (in the form of films or powders) of new compounds—electrides, obtained for the first time on evaporating solutions of solvated electrons. Electrides is the name given to salts in which the localised electrons behave as anions and the positive ions are alkali metal complexes. The salts Cs^+. .(18C6)e^-, where the symbol 18C6 denotes a complex-forming crown compound (a macrocyclic polyether), is an example of an electride.[120] As a result of the strong electron–electron interaction and the delocalisation of electrons, electrides exhibit extremely unusual properties, approaching the properties of metals, including high electrical conductivity and absorption spectra of the plasma type.[42] The hypothesis that electrides are Wigner crystals is of interest.

V. ELECTROCHEMICAL PROPERTIES

Chemically stable systems with solvated electrons include in the first place solutions of metals in ammonia (the counterions in such systems are usually alkali metal ions) and also in aprotic solvents such as hexamethylphosphoramide (HMP), dimethyl sulphoxide, diglyme, etc.

The method of electrochemical generation of solvated electrons in such systems, which makes it possible to investigate e_s under stationary conditions in controlled chemical reactions in the bulk of the solution and on the electrode, is very interesting. Although the electrochemical generation of solvated electrons in ammonia was reported as early as 1948,[121] the qualitative investigation of this process did not begin until the 1970's (see the relevant reviews[24,26]) after the investigation of the characteristics of photoemission into electrolyte solutions.[64,65] Clearly the photoemission and the electrochemical e_s generation processes are in many respects analogous and differ essentially only in the detailed mechanisms of the excitation of the electron from the Fermi level of the metal: in the first case the excitation is optical and in the second thermal.

For high negative potentials of the cathode, the cathodic generation of electrons should be observed theoretically in all electrolytes. However, in fact the actual occurrence of cathodic generation requires that (1) the solution should be stable in relation to the cathodic reduction of positive ions at fairly high negative potentials of the cathode and (2) that the reaction of the electrons in the bulk phase with positive ions should be at least hindered. Otherwise, instead of the cathodic generation of e_s, the reduction of counterions either on the electrode (deposition of the metal) or immediately in the region near the electrode is observed. We may note that a number of workers[24,122] hold the view that many of the known electrochemical reduction reactions proceed precisely via a mechanism involving the generation of e_s with subsequent interaction (in the part of the solution near the electrode) of the solvated electrons and positive ions.

This type of mechanism has been discussed in the literature even for the usual discharge of H^+ ions in the electrolysis of water. However, detailed study has shown that in water the "classical" discharge of H^+ ions nevertheless takes place on the electrode.[24] Among all the solutions, the conditions specified are satisfied best by the aprotic systems enumerated above (HMP, diglyme, etc.). It is therefore not in any way surprising that the greatest number of data on the cathodic generation of e_s have in fact been obtained using HMP, which is a liquid under normal conditions.

In the cathodic generation of e_s, two reaction pathways are possible in principle. In the realisation of the first of these, the electrons of the metal, thermally excited above the level corresponding to the electrochemical potential of the delocalised electron on the "bottom of the conductivity band of the solution",† overcome the surface barrier, move along the conductivity band, and are thermalised and solvated at a certain distance from the electrode. The possibility of the generation of solvated electrons under these conditions is determined by the activated excitation of the electron to the V_0 level. The second reaction pathway involves the tunnel transition of the electrons of the metal to the E_s level of the solvated electrons in solution. The electron must then "tunnel" over a certain distance into the solution. The activation energy for such a process, equal to $E_s - E_F$ (E_F is the Fermi level in the metal), is naturally smaller than the activation energy for the first pathway, but we have here instead kinetic limitations associated with the low probability of tunnelling over comparatively large distances. Clearly, for different potentials and states of the surface of the cathode, one or other mechanism of the cathodic generation of e_s takes place preferentially.

There is experimental evidence for the operation of both mechanisms of the generation of e_s.[24,123,124] In the above studies it was also concluded that there is a possibility of a change in the generation mechanism when the state of the electrode surface changes (the surface is passivated). Indeed, at a fixed potential of the electrode, the formation on the latter of a passivating film increases the tunnelling distance. For a sufficient thickness of the film, the process involving the excitation of the electron to the conductivity band of the solution, whereupon the electron passes over the surface barrier, is more probable.

The study of the anodic oxidation reactions of solvated electrons showed that they are controlled by diffusion and that the oxidation potential depends on the state of the electrode surface. Apart from the discharge of the solvated electrodes on the anode, the polarisation curves for HMP revealed yet another limiting current plateau, corresponding to the discharge of non-paramagnetic complexes containing two electrons and an alkali metal ion. In relation to discharge on the anode, the monoelectrons are significantly more active than the non-paramagnetic complexes;[124] their oxidation potentials differ by approximately 0.5 eV. The study of the anodic reactions of solvated electrons made it possible

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†The very concept of the "conductivity band" in a disordered system with a strong electron–phonon (electron–exciton) interaction requires discussion. Being in a delocalised state, the electron "does not have time" to interact with the slow orientational polarisation of the medium. Here it is more appropriate to speak of the influence of the electronic and nuclear polarisation of the medium, i.e. of the interaction of the electron with high-frequency phonons and excitons, which can be regarded as weak. In this case one can actually use the ideas about the conductivity band developed for ordered media. The validity of the hypothesis of the "bottom of the conductivity band of the solution" has been demonstrated by experiments on photoemission into solutions and from solutions (see Brodskii and co-workers[64,65]).

to estimate accurately their concentrations in solution from the limiting discharge current and to establish, on the basis of the concentration of the electrons, the concentration dependence of the equilibrium "electronic" potential and to calculate the standard potential of the reversible electron electrode in HMP.[124] An analogous study has been carried out also for ammonia.[103]

Investigation of the bulk-phase reactions of cathodically generated electrons is extremely promising. Since solvated electrons are "rapidly moving" species, i.e. have high diffusion coefficients, in many cases it is more convenient to carry out the reaction in the bulk phase by supplying electrons to the latter than to ensure the transport of the reducible species to the electrode. Furthermore, the change in many solvents of the density of the medium near the sites where the electron is localised promotes the mixing of the solution by convection, which also accelerates the reaction in the bulk phase. Solvated electrons, whose standard potential is close to the standard potentials of alkali metal ions, are one of the most powerful reductants and, since they can be generated at large concentrations, it is possible to achieve many reactions with organic compounds which are difficult to reduce. At the present time there already exist many examples of such processes.[24,26,122–124]

VI. PRINCIPAL ENERGETIC CHARACTERISTICS

The following scheme of the states of solvated electrons can be put forward. The delocalised "dry" electron moves along the "conductivity band", whose bottom is at the level V_0 reckoned from the energy level of the electron *in vacuo*. After solvation, accompanied by a possible rearrangement of the medium and the localisation of the electron, the energy of the self-consistent "electron–medium" system is $E^e_s + E^m$, where E^e_s is the energy of the electron and E^m the energy of the reorganised medium. Apart from the ground and delocalised (quasi-free) states of the electron, excited localised states may arise, which can be regarded as resonances in the continuous spectrum of the electron–phonon system. In an optical transition, which proceeds in accordance with the Franck–Condon principle without change in the "slow" coordinates of the medium, the electron passes from the ground state to one of the excited states or to a "band" state. The medium then remains in the initial state and the excited levels are therefore non-equilibrium in nature and their energies, generally speaking, differ from the energies of the corresponding equilibrium levels. We shall denote the "Franck–Condon" excited levels by an asterisk: for example, $(2p)^*$ is the $2p$ state of the electron not adjusted for consistency with the state of the medium and $(2p)$ is the state adjusted for such consistency.

In order to find the difference between the chemical potentials of the delocalised (quasi-free) and localised solvated electrons ($\mu_d - \mu_s$), it is necessary to take into account the entropy factor. When the Boltzmann formula is used, we obtain

$$\mu_d-\mu_s=-E^e-E^m+V_0+kT\ln\left[\frac{(mkT/2\pi h^2)^{3/2}a^3c_s}{c_dg}\right] \cdot \qquad (22)$$

The formula for the chemical potential of an ideal gas was used here for the delocalised electron and the degeneracy factor g, effectively allowing for the change in the number of states of the phonon subsystem on localisation of the electrons, was introduced; the factor a is approximately equal to the average radius of e_s, i.e. corresponds in order of magnitude to the intermolecular distance, and $c_{s(d)}$ is the concentration of localised (delocalised) electrons. We emphasise that the concept of the "solvated electron" refers to the entire many-particle excess electron + medium system. At equilibrium ($\mu_d = \mu_s$), we have

$$c_s/c_d=c(g)\cdot\exp\left(\frac{V_0-E^e_s-E^m}{kT}\right) \qquad (23)$$

and the numerical coefficient $c(g)$ attains 10^3 at room temperature even if $g = 1$. We may note that the possible existence of systems in which the localisation of electrons is favoured by thermodynamic factors when the energy of the localised state exceeds that of the delocalised electron at the bottom of the "conductivity band" follows from the previous treatment. In the description of the interaction with electromagnetic radiation, such a system can be regarded as one with inverse population and laser action is possible in it as a result of the energy of the phonon subsystem.

Table 1. Thermodynamic and energy parameters of solvated electrons determined in different experiments.

Type of experiment	Quantity determined
Measurement of the optical absorption spectrum	Oscillator strength of optical transitions (Refs,22, 90–94]; the position of the absorption maximum (corresponds to the energy differences $E^e_{(2p)*} - E^e_s$ if a discrete level exists and to $\sim 2(V_0 - E^e_s)$ if the spectrum corresponds to the photoionisation of e_s and there are no autoionisation states)
Measurement of the photoconductivity excitation spectrum	Photoconductivity threshold, energies of autoionisation states: $V_0 - E^e_s$, $E^e_{(2p)*} - E^e_s$, etc.
Photoemission into a liquid	Position of the bottom of the conductivity band V_0 (if the emission is into the "band"), the energy E^e_s (if there is a tunnel transition to a bound level)
Cathodic generation	Thermodynamic parameters of the ground state of e_s
Photoemission from the solution to a vacuum (vapour)	The photoemission threshold E^e_s
Thermal emission from the solution to a vacuum (vapour)	Free energy of activation for thermal emission $E^e_s + E^m - T\Delta S$
Dissolution of the metal	Free energy of solvation $E^e_s + E^m - T\Delta S$

Table 1 shows a systematic arrangement of the energy and thermodynamic characteristics of solvated electrons obtained in different experiments. It also includes the differences ΔS between the specific entropies of the delocalised and localised states which can be written in the following form by analogy with Eqn.(22):

$$\Delta S=kT\left[c_s\ln\left(\frac{a^3c_s}{g}\right)+c_d\ln\left(\left(\frac{mkT}{2\pi\hbar^2}\right)^{-3/2}\right)\right] \qquad (24)$$

We may note that we never use the thermodynamic characteristics of the electrons *in vacuo*, because they cannot form a homogeneous equilibrium system *in vacuo*.

A number of comments may be made concerning the amount of information yielded by the different experiments indicated in Table 1. The greatest number of data naturally refer to the spectroscopic characteristics of the solvated electron.

However, when the nature of the transition has been established, these data by themselves say nothing about the energy parameters of the different states of e_s. Only careful analysis of the spectroscopic data using the sum rules, additional thermodynamic information, and other data would make it possible to estimate the energy parameters of e_s from the optical spectra. For example, in the measurement of the spectra of e_s in ammonia–alcohol and hydrazine–alcohol mixtures the superficially strange conclusion is reached that the electrons "solvated in ammonia and hydrazine", absorbing at lower frequencies than the "alcoholic" electrons, are favoured by energy factors.[80–82] However, if it is assumed that the spectrum of e_s in ammonia is determined by transitions between bound states and the spectrum of the electron in alcohol is determined by transitions of the "bound state–conductivity band" type then the observed facts can find a natural explanation.

The study of photoemission from a metal to a vacuum, an electrolyte, or a dense electrolyte vapour can yield much information about the position of the solvated electron at the bottom of the conductivity band as a function of the density of the electrolyte.[64,83] Joint measurements of the absorption and photoconductivity spectra and the spectra of the photoemission from the metals to the solution and from the solution to a vacuum would then make it possible to obtain all the energy characteristics of the ground and excited states of e_s. Unfortunately at the present time there are no photoconductivity data at all and the remaining data have been obtained in different systems and are non-systematic.

There exist certain data on thermal emission from solutions,[126] but these have been subjected to a justified criticism[64] in view of the lack in the relevant communication of information about the temperature dependence of the density of the vapour phase (and hence about the energy characteristics of the electron in it).

Table 2. Certain energy characteristics of e_s.

Characteristic	Medium		
	ammonia	HMP	water
Maximum of absorption spectrum, eV	0.88 [14]	0.45 [129]	1.72 [16]
Position of bottom of conductivity band, eV	—	—0.9 [128]	—1.3 [128]
Solvation energy, eV	1.7 [127]	1.0 [126]	1.5 [128]
Solvation entropy, J mol^{-1} K^{-1}	154 [103]. 47 [130]	—	49 [130]. 12 [101]
Threshold of photoemission from the solution to a vacuum, eV	1.53 [131]	0.9 [131]	—

Note. The numerals in square brackets represent references (Ed.of Translation).

Presumably experiments on the electrochemical generation of e_s [24,108,111,124] can yield the most accurate thermodynamic data. The same may be said of data on the thermodynamics of electrochemical reactions obtained from measurements of the e.m.f.'s of cells containing solvated electrons. Unfortunely, the majority of experiments on the cathodic generation of e_s have been carried out in HMP and the e.m.f. data have been obtained solely for electrons in ammonia. Altogether, there exist at the present time an enormous number of different experimental data referring to different systems but a sufficiently complete set of information has been accumulated for only one system—that in ammonia.

Table 2 summarises the known energy and thermodynamic characteristics of solvated electrons in a number of solvents. The very large positive entropies of solvation of the electron in ammonia and HMP, greatly exceeding the entropies of solvation of ions in these solvents, are noteworthy.# Furthermore, the similarity of the heats of solvation of the electron in HMP and ammonia to the thresholds of the photoemission of electrons from these solvents, i.e. the closeness of the value of E^m to zero, is striking, although the photoemission data for these solvents should be regarded as estimates only. Hitherto no experiments have been carried out on the photoconductivity of electrons solvated in liquid solvents, although there is a genuine need for them. Furthermore, from our standpoint, the lack of photoconductivity data to a large extent vitiates the existing extensive information about the spectra of e_s.

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As shown in the introduction, different physicochemical effects associated with the solvated electron have come to the centre of attention during different periods. In particular, during the 1960's, the role of solvated electrons in the radiation chemistry of aqueous systems aroused special interest. At the present time, the study of the details of the dynamics of various reactions involving e_s, especially reactions with charge transfer in polar solutions and vitreous matrices, electrochemical reactions, and complex biochemical processes, including the role of e_s in photosynthesis, is of greatest current interest. Comparison of the data obtained with theoretical conclusions provides unique possibilities for testing various concepts in chemical kinetics.

It follows from the foregoing that numerous problems concerning the characteristics of e_s have not yet been solved. It is especially important to determine theoretically and experimentally the dependence of the transport properties of the solvated electron on temperature over the widest possible range of the latter and to study the photoconductivity. The possibilities of investigating the chemical and electrochemical reactions of solvated electrons and of the unusual compounds such as the electrides formed with their participation have not been fully utilised. There is no doubt that the interest in the role of the solvated electron in photosynthetic processes and in the transfer of excitations in biological systems will grow. Finally, in the immediate future the quantum chemistry of e_s should develop further. It is significant that the theoretical study of an exotic anion such as e_s makes it possible to compare effectively and to assess the approaches developed both in quantum chemistry and in the electronic theory of disordered media.

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The Cleavage of the Carbon-Carbon Bond in Carbonyl Compounds and Alcohols under the Influence of Bases

G.A.Artamkina and I.P.Beletskaya

The characteristics of the cleavage of the carbon-carbon bond in carbonyl compounds and alcohols of different types are considered. It is shown that the ease of dissociation of this bond is determined primarily by the stability of the carbanion formed. Among other factors, the nature of the solvent, the base, and the counterion are important. The importance of the latter factor has the greatest influence on the stability of the O-M bond in alcohols and hydroxycarbonyl compounds. The bibliography includes 281 references.

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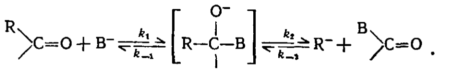
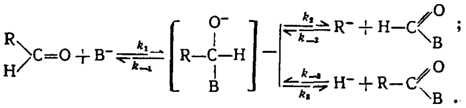
I. INTRODUCTION

The heterolytic cleavage of the carbon–carbon bond is a fairly rare although important reaction in organic chemistry. Such cleavage is usually associated with the formation of carbanions (in a free or cryptoanionic state) and proceeds reversibly, so that, if the stability of the carbanions is insufficient, the occurrence of the reaction requires the presence of special carbanion acceptors. The reactions considered here include the following:

1. The reaction of carbonyl compounds with bases:



In the general case we have here competition between the abstraction of B^- and R^- (stages with the rate constants k_{-1} and k_2). The bases employed in this reaction are usually OH^- or OR^-, but amides and other nucleophiles, including carbanions, can also be used. We may note that for aldehydes there is also the possibility of the abstraction of a hydride ion (stage with the rate constant k_3):

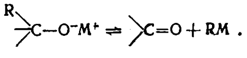


The reactions of the type considered include also the retro-Claisen condensation, in particular, the so called acid cleavage of the acetoacetic ester.

2. Decarboxylation of carboxylic acids with participation of the anion:

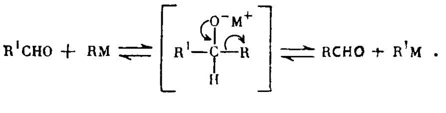
$$RCOO^-M^+ \rightleftharpoons R^-M^+ + CO_2\ .$$

3. Decomposition of carbinolates (alkoxides)—the reaction which is the opposite of the addition of organometallic compounds to the carbonyl group—the most important process leading to the formation of the carbon–carbon bond:



Such reactions include the retroaldol condensation (the reverse reaction, i.e. the aldol condensation, involves the addition of an alkali metal enolate to the carbonyl group).

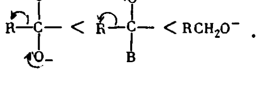
Naturally, the decisive factor in all the reactions considered is the stability of the carbanion split off, so that, in the presence of several substituents in the carbinolate RR^1R^2COM, the C–C bond ruptured is that having the substituent which corresponds to strongest CH acid RH. Thus, in principle, it is possible to formulate the equilibrium in which one carbanion induces the displacement from an aldehyde or ketone another more stable carbanion:



$$R^1CHO + RM \rightleftharpoons \left[R^1-\overset{\overset{\displaystyle O^-M^+}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-R \right] \rightleftharpoons RCHO + R^1M\ .$$

However, there exist also other factors, which likewise determine the possibility of the cleavage reactions considered. These are primarily the nature of the base and the solvent and, when a specific type of base is used, the nature of the counterion. The role of the last factor is associated with the difference between the effects of the counterion on the ease of ionisation of the O–M and B–M bonds and is determined by the exclusively strong dependence of the stability of the O–M bond (in relation to ionisation) on the nature of M (which is much more pronounced than in the case of, for example, the C–M bond).

As was to be expected, the free anion is cleaved most readily. If anions such as the carbinolate, the tetrahedral anionic intermediate formed when the base adds to the carbonyl group, as well as the dianion arising on treatment with an excess of alkali are compared, then their stabilities are seen to vary in the sequence



$$R-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle O^-}{|}}{C}}- < R-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle B}{|}}{C}}- < RCH_2O^-\ .$$

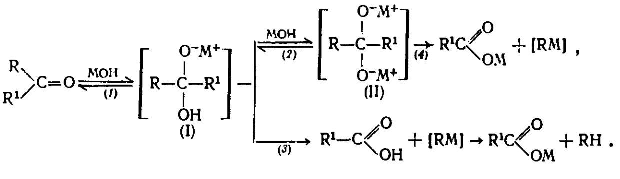
Thus it is possible to trace the general characteristics of the reactions involving the cleavage of the C–C bond occurring in compounds of different classes and having at first sight little in common. The present review is devoted to the analysis of the available data concerning the influence of the stability of the carbanion, the nature of the solvent, and the nature of the counterion on the ease of cleavage of the carbon–carbon bond.

II. THE CLEAVAGE OF KETONES AND ALDEHYDES BY BASES

1. General Considerations

Ketones are usually cleaved by bases with difficulty. An exception is ketones containing in the α-position strong electron-accepting groups, for example, NO_2 or SO_2,[1] quaternary ammonium,[2] and keto- or ester groups.[3] The last case represents the well known reaction involving the acid cleavage of β-dicarbonyl compounds.[4] Trihalogenomethyl ketone and trihalogenoacetaldehydes are readily cleaved (haloform cleavage reaction).[5] The study of the kinetics of the cleavage of such carbonyl compounds by alkalis in aqueous solution showed that all these processes can be represented by a single scheme (Scheme 1):[1-3]

Scheme 1

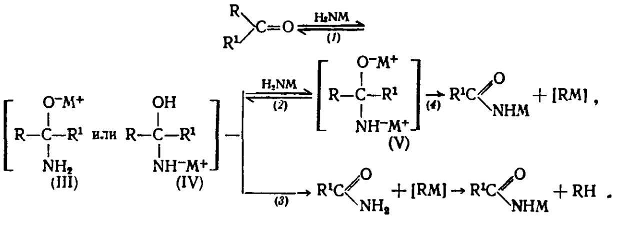


where R is a stronger electron-accepting group than R^1.

Kinetic studies have made it possible to postulate that, depending on the nature of the carbonyl compound, the rate-limiting stage can be both stage (1), involving the addition of the hydroxide anion to the carbonyl group (for example, for nitroacetone, ω-nitroacetophenone,[1] αα-dimethylacetophenone,[3] and thienyltrifluoroacetone[1,6]) and the formation of the dianion (II) (for ketoalkylpyridinium salts and sulphonylketones[1,2]) or its decomposition (for example, for acetylacetone, methylacetylacetone,[3] chloral hydrate, and 2,6-dihalogenobenzaldehydes[7,8]).

Potassium or sodium amides in liquid NH_3 or in aromatic hydrocarbons such as benzene, toluene, and xylenes (Haller–Bauer cleavage) are frequently used as bases for the cleavage of ketones.[9-11] The fundamental scheme for these processes (Scheme 2) is analogous to that presented above:[9,12,13]

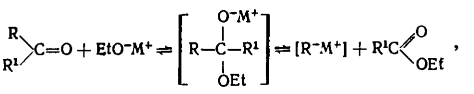
Scheme 2



It follows from Schemes 1 and 2 that the first stage in the cleavage of carbonyl compounds by bases involves the addition of bases to the carbonyl group with formation of the intermediate (I) or (III)/(IV). Adducts of type (III) have been frequently isolated in reactions with NH_3 or amides at low temperatures; on decomposition with water, they regenerated the initial ketones.[14-17] Similar adducts with alkalis, alkoxides, and other bases are probably less stable. We may note that the adducts of formaldehyde with hydroxide and methoxide ions have been recently detected in the gas phase.†[18]

The majority of cleavage reactions of carbonyl compounds apparently require the formation of the dianions (II) or (V), which follows from kinetic data (second order with respect to the alkali).[1-3,8,12,13] The heterolysis of such dianions should naturally proceed more readily than that of the monoanions. The formation of the dianions is indicated also by the fact that, in the absence of a proton donor, the hydrocarbon RH is not formed.[20] When fairly stable carbanions R^-, such as the nitromethyl or trifluoromethyl carbanions, are formed, the monoanion (I) can apparently also undergo heterolysis;[1] in this case it may be protonated by the acid formed, giving rise to the hydrocarbon RH.

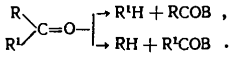
When carbonyl compounds are cleaved by alkoxides in alcohols, there is a possibility of the formation of only the monoanion, but it has been demonstrated nevertheless that acetylacetone and 2-ketoalkylpyridinium salts are readily cleaved under these conditions:[21]



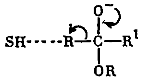
$$\begin{array}{c}R\\R^1\end{array}\!\!>C{=}O + EtO^-M^+ \rightleftharpoons \left[R{-}\overset{O^-M^+}{\underset{OEt}{C}}{-}R^1\right] \rightleftharpoons [R^-M^+] + R^1C\begin{array}{l}{\nearrow}O\\ \searrow OEt\end{array} ,$$

$$[R^-M^+] + EtOH \rightarrow RH + EtO^-M^+ .$$

In the general case, when asymmetric ketones are cleaved by bases, there is a possibility of the formation of a mixture of two acids (or their derivatives) and two hydrocarbons:[9,22,2

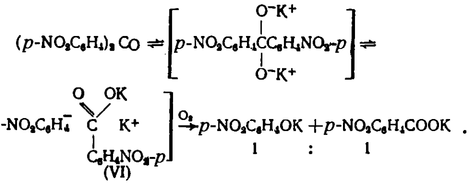


The mode of reaction is determined by the relative stabilities of the carbanions R^- and $(R^1)^-$—the most stable carbanion is split off. Therefore, if the stabilities of the carbanions are approximately identical, i.e. the pK_a of the corresponding RH and R^1H are similar, then a mixture of four products is formed. The ease of cleavage of carbonyl compounds is also determined by the stabilities of the carbanions produced (see below). The question arises whether these reactions lead to the formation of the carbanion R^- as a kinetically independent species or is it possible, as has in fact been suggested,[24] that the product RH is formed as a result of the attack by the proton-donating compound (SH) directly on R in the adduct:

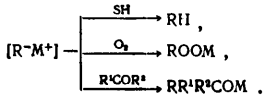


According to Artamkina et al.,[20] the ion pair VI participates in the reaction, as shown in Scheme 3 for the cleavage of $(p\text{-}NO_2C_6H_4)_2CO$, where oxygen functions as the trapping agent for R^-:

Scheme 3



Naturally, the organometallic compound RM itself can also be formed in these reactions if R^- is a sufficiently stable carbanion. On the other hand, in the majority of cases the reaction requires the presence of a suitable compound functioning as the trapping agent for the carbanion:



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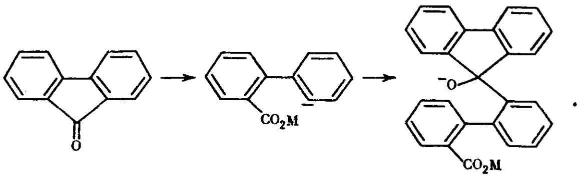
† The adduct of an alkoxide with *NN*-dimethyltrifluoroacetamide has been recently detected in solution.[19]

The cleavage of carbonyl compounds is usually carried out in aqueous or alcoholic solutions and the trapping is a proton-donating compound. This role can sometimes be assumed by O_2.[20] In the absence of a proton donor, the ketone itself can act as the trapping agent. For example, in the cleavage of benzophenone and its *pp*′-difluoro-derivative, triarylcarbinols have been obtained in 75–86% yield by treatment with KOH in dimethoxyethane (DME):[20]

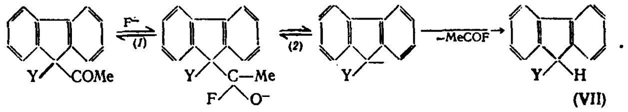
$$[XC_6H_4^-K^+] \xrightarrow{(XC_6H_4)_2CO} (XC_6H_4)_3COK,$$
$$X = H,\ p\text{-F}.$$

The formation of small amounts of triarylcarbinols (X=H or *p*-Cl) has also been noted in other studies.[23–26] A similar reaction has likewise been observed in the cleavage of fluorenone;[27–29] the yield of the carbinol reached 94% in some cases:[28]



In the absence of carbanionic trapping agents, the stages (3) and (4) (in Schemes 1 and 2) are as a rule reversible and the process as a whole therefore becomes reversible. This has been clearly demonstrated for the cleavage of 9-substituted 9-acetylfluorenes by the fluoride ion (KF-18-crown-6 ether or Bu_4NF/SiO_2) and it was shown that both stage (1) and stage (2) (Scheme 4) are reversible:[30]

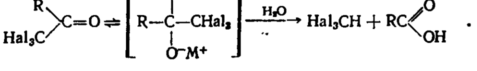
Scheme 4



When Y = CN, the equilibrium is strongly displaced towards the reaction products. Subsequent hydrolysis showed that the yield of RH (VII) diminishes in the sequence Y = CN > $PhCH_2$ > Me and on passing from a non-polar to a polar solvent.[30]

Specific examples of the cleavage of carbonyl compounds by various bases are examined below.

2. The Haloform Reaction



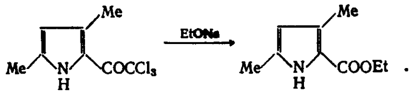
$$\begin{matrix}R\\Hal_3C\end{matrix}\!\!>C{=}O \rightleftharpoons \left[R-\overset{\displaystyle O^-M^+}{\underset{\displaystyle O^-M^+}{C}}-CHal_2\right] \xrightarrow{H_2O} Hal_3CH + RC\!\!<\!\!\begin{matrix}O\\OH\end{matrix}\ .$$

Such reactions occur frequently and usually readily,[5] because trihalogenomethyl anions are fairly stable (the pK_a of the corresponding CH acids are 13.7–15.5 [31]). The cleavage sometimes occurs simply on treatment with water, as happens, for example, for hexabromo- and hexachloro-acetones,[32,33] but usually bases have to be employed. Thus ααα-trichloroacetophenone can be heated for 7 h at 170 °C without change, but in the presence of catalytic amounts of MeCOOK it is immediately cleaved.[34] αα-Dibromoacetophenone is cleaved on boiling with a sodium carbonate solution.[35] Perfluoro-t-butylphenyl ketone is entirely stable, but decomposes rapidly in the presence of catalytic amounts of CsF in DME:[36]

$$PhCOC(CF_3)_3 \xrightarrow{F^-} PhCOF + (CF_3)_3C^- \xrightarrow[-F^-]{} (CF_3)_2C{=}CF_2\ .$$

However, KOH and NaOH are usually employed as bases in the haloform reaction, $Ca(OH)_2$ and $Ba(OH)_2$ being more rarely used.[5]

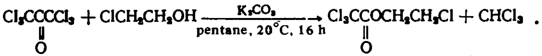
The haloform reaction is used to synthesise bromoform and iodoform, the determination of the structures of organic compounds, and sometimes for the synthesis of acids or their esters.[5] For example, ferrocenemonocarboxylic and ferrocenedicarboxylic acid are obtained by treating mono- or diacetylferrocenes with hypohalites.[37] Aliphatic acids with branched groups of the type of Me_3CCOOH and Me_3CCH_2COOH or unsaturated acids, which are sometimes difficult to obtain in other ways, can be synthesised with the aid of this reaction; in the presence or alcohols, esters are produced,[34,38] for example:



Phenylesters can also be obtained by a similar procedure:[38]

$$PhCOCCl_3 - \begin{cases} \xrightarrow{PhOH,\ KOAc} \underset{80\%}{PhCOOPh}, \\ \xrightarrow{(o,\ p)\text{-}MeC_6H_4OH} \underset{90\%}{PhCOOC_6H_4Me\text{-}(o,\ p)}. \end{cases}$$

Hexachloroacetone is used for the trichloroacetylation of alcohols and phenols:[39–41]



$$\underset{\displaystyle \overset{\|}{O}}{Cl_3CCCCl_3} + ClCH_2CH_2OH \xrightarrow[\text{pentane, 20°C, 16 h}]{K_2CO_3} \underset{\displaystyle \overset{\|}{O}}{Cl_3CCOCH_2CH_2Cl} + CHCl_3\ .$$

In aprotic dipolar solvents such as nitromethane,[40] dimethyl sulphoxide (DMSO), dimethylformamide, (DMF), pyridine, and hexamethylphosphoramide (HMP),[41] the reaction can be carried out in the absence of a catalyst. DMF proved to be especially effective.[41]

The decomposition of hexachloro- or hexabromo-acetone is also induced by ammonia[33] and amines, even aromatic amines:[42]

$$CCl_3COCCl_3 + RC_6H_4NH_2 \xrightarrow[20-80°]{H_2O} Cl_3CCONHC_6H_4R,$$
$$R = H;\ MeO,\ Me,\ OH,\ Cl\ .$$

The trichloroacetylation of peptides has been carried out in an analogous manner.[43]

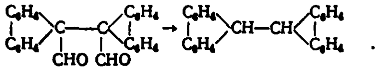
On treatment with hypohalites, carbonyl compounds of other classes are also cleaved—α-ketoesters, β-diketones, or β-ketoesters. In essence, these reactions are analogous to the haloform cleavage reactions. Some of them have been described in a review.[5]

3. The Cleavage of Aldehydes by Bases

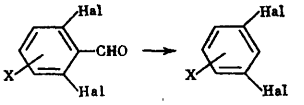
Aldehydes without α-hydrogen atoms usually enter into the Cannizzaro reaction,[44] but there are a number of exceptions whereupon treatment of aldehydes with alkali results in their cleavage:

$$RCHO + MOH - \begin{cases} \xrightarrow[(1)]{} RCH_2OH + RCOOH, \\ \xrightarrow[(2)]{} RH + HCOOH\ . \end{cases}$$

Naturally, the second mode of reaction occurs in those cases where the Group R is sufficiently electron accepting. The well-known examples of such reactions are the cleavage of chloral,[45] bromal,[46] mixed bromochloroacetaldehydes,[47] and even aldehydes containing the SO_3K or SO_3H group in the α-positions[48–51] on treatment with alkalis. On heating with 20% KOH (130 °C, 5 h)[52,53] or with alcoholic KOH (120 °C, 5 h),[54] triphenylacetaldehyde is cleaved to triphenylmethane. Aldehydes containing an acetylenic group in the α-position (propargyl, phenylpropargyl,[55] and tetrolic[56] aldehydes) are cleaved by dilute KOH solutions at 20 °C. Other examples of the ready cleavage of aldehydes, for example, bisdiphenylene succinic aldehyde[52] or trichloroacrolein,[57] can also be quoted:



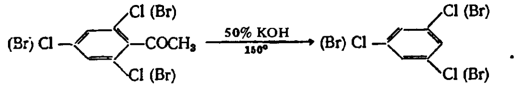
In the series of aromatic aldehydes, an essential condition for their cleavage in an alkaline medium is the presence of two electron-accepting substituents, and halogen atoms, for example, must be in the *ortho*-positions. 2,6-Dihalogenobenzaldehydes are cleaved by refluxing with 50% KOH and under these conditions the aromatic ring can contain also other substituents, including electron-donating substituents (Me, MeO):[58]



Dinitrobenzaldehydes react much more readily and in this case not only 2,6-dinitro- but also 2,4-dinitro-benzaldehydes are cleaved.[59] Trinitrobenzaldehyde is cleaved especially easily—it is sufficient to heat it with alcoholic solutions of NaOH or NH_3, Na_2CO_3 (10%), or even aniline (the yield of trinitrobenzene is up to 95%).[59] Thus the general trend is evident: the reaction is faster, the more stable the carbanion formed. A single chlorine atom in the *ortho*-position in benzaldehyde is insufficient to alter the mode of reaction—the usual Cannizzaro reaction takes place in this case.[58]

4. The Cleavage of Ketones by Alkalis and Alkoxides

As will be seen from the data presented below, the cleavage of ketones obeys the rules which have been noted above for aldehydes. Thus acetophenone and its monochloro-derivatives are cleaved by alkali with difficulty. It is of interest that the cleavage proceeds with abstraction of the methyl and not the phenyl group.[60] It may be that the ease of protonation of the more nucleophilic group plays a role in this case. The reaction is accompanied by charring and the yield of benzoic acids is insignificant.[60] Even when acetophenone is heated with KOH melt at 220–250 °C, only 20% of benzoic acid is formed.[61] The same has been observed for methylacetophenones.[60] The situation changes sharply when two chlorine or bromine atoms are introduced in the *ortho*-positions in the benzene ring; the process proceeds even more readily with 2,4,6-trichloro-, 2,4,6-tribromo-, and 2,3,4,5,6-pentachloro-acetophenones (50% KOH, 150 °C), but the products of these reactions are halogenobenzenes and not benzoic acids:[60]



Naturally 2,4,6-tribromo-ααα-trichloroacetophenone gives rise to 2,4,6-tribromobenzoic acid on cleavage.[62]

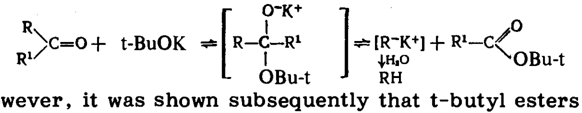
Acetophenone and other enolisable ketones undergo the condensation reaction more readily than the cleavage reaction and cleavage has therefore been investigated for non-enolisable ketones, in the first place benzophenone and its derivatives.[22,23,63–67] Benzophenone was cleaved as early as 1849 by fusing it with KOH at 260 °C:[63]

$$Ph_2CO + KOH \xrightarrow{[illegible]} PhCOOK + PhH\ .$$

Under just as severe conditions, *mono*- and di-methylbenzophenones are cleaved with formation of toluic acids.[64–67] The introduction of even one chlorine atom in the *ortho*-position in the benzene ring proved to be sufficient to increase significantly the rate of reaction, whereupon chlorobenzene and benzoic acid are formed.[23] The influence of chlorine is so great that 2,4,6-trichlorobenzophenone is cleaved even by refluxing for 2 h with a dilute (20%) alcoholic solution of KOH.[68] Benzophenone itself and many of its substituted derivatives (with methyl and halogeno-substituents) are reduced under these conditions to diphenylmethanols, while benzophenones with strong electron-donating substituents do not react or char.[24,68,69] It is noteworthy that at the present time a method is available for the cleavage of benzophenone under much milder conditions—refluxing the ground KOH in DME or tetrahydrofuran (THF).[20] Fluorenone and its substituted derivatives are cleaved in a KOH melt[27] or in diphenyl ether.[70]

In recent years, t-BuOK has been most widely used for the cleavage of ketones, usually in aprotic dipolar solvents.[25,26,71–76] This method was proposed by Swan as early as 1948.[24] Ether, dioxan, pyridine, DMSO, HMP, and DME and also benzene and hexane can be used as solvents in these reactions. A very important factor is the presence of small amounts of water in the reaction mixture. Careful experiments have shown that t-BuOK : H_2O = 3 : 1 is the optimum ratio. In the absence of a proton source, the yields of acid are insignificant (the reaction usually does not occur at all). The mechanism initially proposed by Swan[24] (Scheme 5) includes the attack by t-BuOK on the ketone; water serves as the trapping agent for the carbanion and generates under these conditions the OH^- anion, which is essential for the hydrolysis of the t-butyl ester:

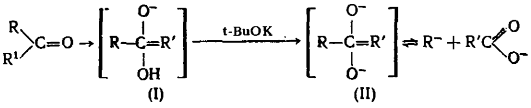
Scheme 5



$$RR^1C{=}O + t\text{-}BuOK \rightleftharpoons \left[R{-}\overset{O^-K^+}{\underset{OBu\text{-}t}{C}}{-}R^1\right] \rightleftharpoons \underset{\substack{\downarrow H_2O\\ RH}}{[R^-K^+]} + R^1{-}C(=O)OBu\text{-}t\ .$$

However, it was shown subsequently that t-butyl esters are not intermediates in these reactions[73] and an alternative mechanism (Scheme 6) was therefore proposed in which the carbonyl group is initially attacked by the OH^- anion with formation of the adduct (I), while t-BuOK abstracts a proton from it, affording the dianion (II):[25,73,74,76]

Scheme 6

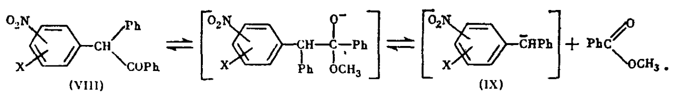


$$RR^1C{=}O \rightarrow \underset{(I)}{\left[R{-}\overset{O^-}{\underset{OH}{C}}{=}R'\right]} \xrightarrow{t\text{-}BuOK} \underset{(II)}{\left[R{-}\overset{O^-}{\underset{O^-}{C}}{=}R'\right]} \rightleftharpoons R^- + R'C(=O)O^-\ .$$

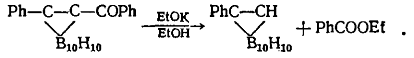
In this version, the role of water consists in generating the hydroxide from t-BuOK. There exists yet another point of view on the mechanism of this reaction—the 3 : 1 : 1 t-BuOK–t-BuOH–H_2O mixture gives rise to an aggregate, which is soluble in organic solvents and in which OH^- is only slightly solvated and is therefore extremely reactive. In this case KOH should cleave ketones in aprotic solvents also in the absence of the t-BuOK–t-BuOH mixture. Indeed, a suspension of KOH, obtained by adding water to an excess of KH in THF, cleaves nortricyclanone in 2 h at 30 °C.[73] However, as mentioned above, ground KOH in THF or DME cleaves even benzophenone under relatively mild conditions.[20] Other di- and tri-cyclic ketones are cleaved in the t-BuOK–H_2O–aprotic solvent system. The authors believe that the driving force of their cleavage is the removal of strain from the system and the formation of stable cyclopropyl and allyl carbanions.[71–73] According to this view, camphenilone and fenchone, which are less strained than, for example, nortricyclanone, dehydronorcamphor, or 7-oxonorbornene, are not cleaved or are cleaved with difficulty.[72] The possibility of the cleavage of ketones such as $PhC(Me_2)COPh$ or $MeOC.(Me_2)COPh$ is also explained by the elimination of steric strain.[77,78]

We may note that dehydronorcamphor, which is an enolisable ketone, is fairly smoothly cleaved by t-BuOK.[71,73,79] Yet another interesting example is the cleavage of α-(*p*- and o-nitrophenyl)deoxybenzoins (VIII), which leads to the formation of benzoic acid and products of the further reaction of the carbanions (IX)—substituted anthranilic acid derivatives and tetraphenylethanes (Scheme 7):[80]

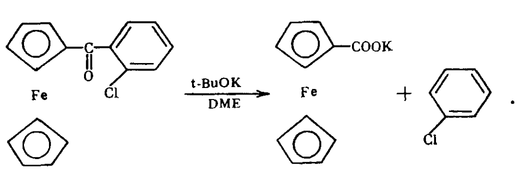
Scheme 7



Ketones of the carbaborane series are readily cleaved by treatment with EtOK in ethanol,[81] because the carbaborane formed is a fairly strong CH acid ($pK_a \cong 18$):[31]


$$\underset{B_{10}H_{10}}{\mathrm{Ph{-}C{-}C{-}COPh}} \xrightarrow[EtOH]{EtOK} \underset{B_{10}H_{10}}{\mathrm{PhC{-}CH}} + \mathrm{PhCOOEt}\ .$$

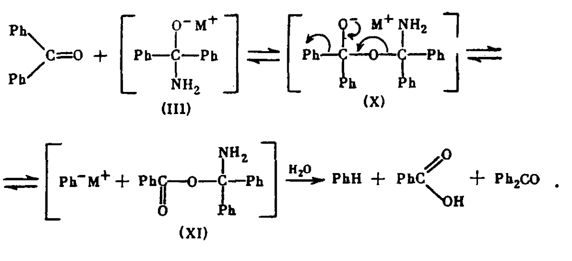
The t-BuOK–DME system has been used for the synthesis of carboxylic acids of the ferrocene and cymantrene series:[82]



5. The Cleavage of Ketones by Alkali Metal Amides

Potassium amide in liquid ammonia does not cleave benzophenone,[12,13] but it does partly cleave benzopinacol[83] and readily cleaves o-halogenobenzophenones.[12,13,17,84] Under more severe conditions, i.e. on refluxing ketones with $H_2NK.(H_2NNa)$ in toluene or xylene, both Ph_2CO and its *ortho*, *para*, and *meta*-substituted derivatives (with the Me, Cl, and Br substituents) are cleaved.[9,85] As a rule, when ketones are cleaved by alkali metal amides, not only amides but also the corresponding acids are formed.[9,12,84] Under the mild conditions used in the isolation of the reaction products, the amide cannot hydrolyse to the acid. The acid is apparently formed in the course of the reaction itself. It has been suggested that the mechanism of the formation of acids on cleavage of ketones by alkali metal amides[12] is analogous to the mechanism of the formation of benzilic acid on treatment of benzil with H_2NNa or RO^- in aprotic solvents.[86] The anion (III) acts as a base, attacking a second ketone molecule, and the heterolysis of the intermediate adduct (X) affords compound (XI), which is converted on hydrolysis into benzoic acid (Scheme 8):

Scheme 8



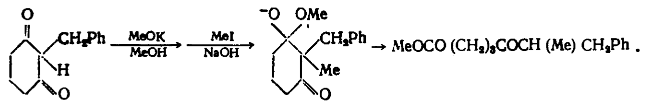
We may note that the intermediate formation of o-halogenophenyl anions has been demonstrated in the reaction with o-halogenobenzophenones.[12,13]

6. The Cleavage of β-Dicarbonyl Compounds

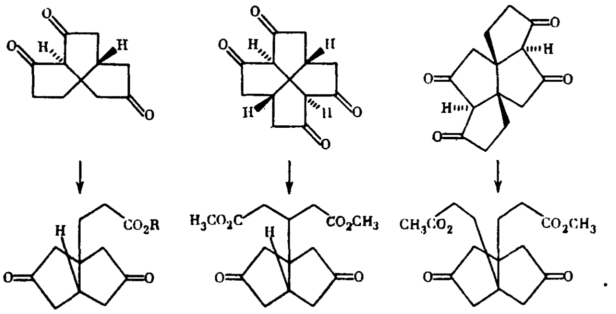
The best evidence that β-dicarbonyl compounds are cleaved by bases in the keto-form is probably provided by the finding that αα-disubstituted β-diketones or β-ketoesters, which are incapable of enolisation, are cleaved most readily.[3,87,88] It has been convincingly demonstrated for thenoyltrifluoroacetone that the enolate is stable in an alkaline medium and that the corresponding hydrate decomposes rapidly.[6] The stage involving the protonation of the enolate of the β-dicarbonyl compound can therefore become important for acid substrates which exist in the enolic forms in alkaline solutions. This situation obtain, for example, in the alkaline cleavage of aroylacetaldehydes, which are fully enolised in 0.1–1 M NaOH solutions:[89]

$$ArCOCH_2CHO + HO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArCOCH{=}CHO^-\ .$$

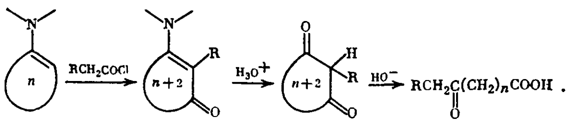
The cleavage of β-dicarbonyl compounds is used fairly often in synthesis.[4,90–92] This method is most important for the series of cyclic β-diketones, where it is used to synthesise oxocarboxylic acids:[4,90–92]



Recently this method has been used to cleave standard tri- and tetra-spiro-β-diketones:[95]



As an example, one may also quote the synthesis of 13-keto-acids, including the reaction of 1-morpholinocyclododecene with an acid chloride and the subsequent cleavage of the 1,3-diketone in an alkaline medium:[93,94]

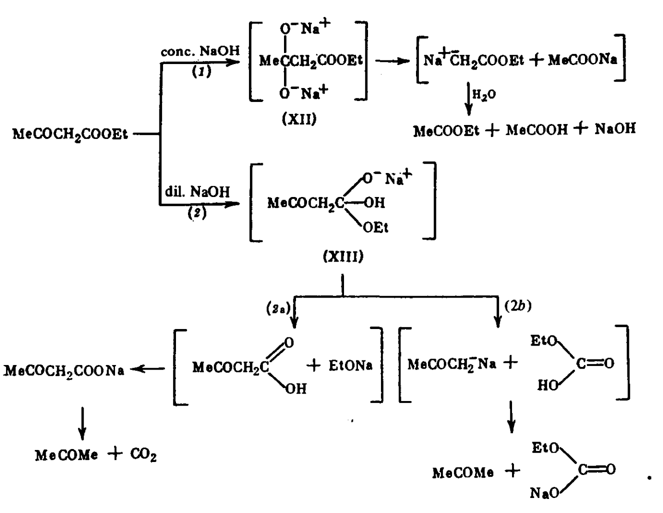


Dibasic ketoacids can be obtained by the reaction of an enamine with the chloride of a dibasic acid.[93,94]

The cleavage of β-dicarbonyl compounds in an alkaline medium is frequently an undesirable side reaction in the alkylation of β-diketones or β-ketoesters. However, the cleavage can be reduced to a minimum by carrying out the reactions at low temperatures, using sterically hindered bases, for example, t-BuOK in t-BuOH, or using NaH in aprotic dipolar solvents.[4]

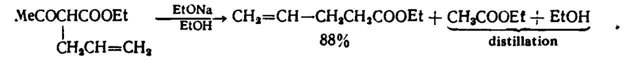
An unusual problem arises in the so called acid cleavage of acetoacetic ester and its analogues (the reaction which is the opposite of its synthesis, i.e. is the retro-Claisen condensation), which is always accompanied by the formation of ketones (ketone degradation) (Scheme 9).

Scheme 9



The first of these reactions involves the addition of the alkali to the keto-group [the adduct (XII)], which should proceed more readily than the addition to the ester group [the adduct (XIII)]. Nevertheless, both reactions [(*1*) and (*2*)] take place almost simultaneously. A possible explanation of this finding is that the dissociation of the C–C bond requires as a rule the formation of the dianion, which is indicated by the second (or higher) order of the reaction with respect to the alkali, while the cleavage of the C–O bond (hydrolysis) can occur in the monoanion. In fact, the intermediate (XIII) can decompose not only via the hydrolysis stage (*2a*) but also via the other pathway (*2b*), especially since this entails the formation of the acetonyl carbanion, which is more stable than the ethyl acetate anion [pK_a(MeCOMe) = 20 and pK_a(Me.COOEt) = 24 [31])]. The operation of this pathway [pathway (*2b*) as well as pathway (*1*) should be promoted by concentrated alkali. It may be that the high reactivity of the keto-group has an effect in the competition between pathways (*1*) and (*2b*).

In practice, the cleavage of dialkyl- or even monoalkylacetoacetic esters at the carbonyl group can be successfully achieved when the reaction is carried out in the presence of an excess of alcohol with catalytic amounts of an alkoxide and with continuous distillation of ethyl acetate from the reaction mixture,[92,96] for example:



$$\underset{\displaystyle CH_2CH{=}CH_2}{MeCOCHCOOEt} \xrightarrow[EtOH]{EtONa} \underset{88\%}{CH_2{=}CH{-}CH_2CH_2COOEt} + \underbrace{CH_3COOEt + EtOH}_{distillation}\ .$$

It is noteworthy that unsubstituted β ketoesters are not cleaved under these conditions but are converted into enolates, which are fairly resistant to the action of bases.

III. DECARBOXYLATION OF CARBOXYLIC ACIDS AND DEALKOXYCARBONYLATION OF ESTERS

The decarboxylation of carboxylic acids and their derivatives is an important process both in synthetic organic chemistry[97–99] and in biochemistry (the latter applies mainly to the decarboxylation of β-ketoacids [100,101]) and this is why much attention has been devoted to its investigation. The unimolecular thermal decarboxylation of acids, involving the formation of a carbanion, has been thoroughly studied:[97]

$$RCOOH \rightarrow R^- + CO_2 + H^+ .$$

Both the neutral acid and its anion or zwitter-ion, for example in the case of acids of the pyridine series, can be decarboxylated.[97] However, we shall not be interested in the decomposition of the carboxylate ion, which may arise both on treatment of the acid with bases and as a result of the dissociation of the acid. It is therefore natural that, when one is dealing with the decarboxylation of neutral acid, one has in mind fairly strong acid and fairly polar solvents. The decomposition of carboxylate ions leads to carbanions, whose formation has been unambiguously demonstrated with the aid of electrophilic trapping agents—bromine, aldehydes, ketones, nitro-compounds, D_2O, etc.[97]

1. Decarboxylation of Monocarboxylic Acids

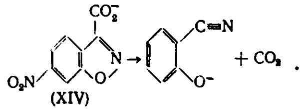
Fairly strong acids such as trihalogenoacetic, 2,4,6-trinitrobenzoic, and α-nitrocarboxylic acids are almost fully dissociated in aqueous solutions even in the absence of bases and it has been shown that they are decarboxylated in the anionic forms:[102–111]

$$RCOO^- \rightarrow R^- + CO_2\ .$$

This has been confirmed by the identity of the activation energies for the decarboxylation of the acids and their salts. In non-aqueous solvents, where the acids are insignificantly ionised, the rate of reaction after the addition of the base is proportional to the concentration of the anion formed. The unionised acids are entirely stable.[102–111] Although water promotes the dissociation of acids and salts, which should facilitate the decarboxylation, it can also stabilise the carboxylate anion as a result of solvation. Indeed, it has been shown that an increase of the fraction of ethanol or formamide in water up to a certain concentration increases the rate of decarboxylation of CCl_3CCOH or its sodium salt.[104,106] Analogous behaviour has been observed for trinitrobenzoic acid after the addition of ethanol or dioxan to the aqueous solution.[108,109] In the decarboxylation of (4-chlorophenyl)-α-cyanoacetate anion, the rate increases sharply in alcohol and increases almost by a factor of 3000 in dioxan compared with water.[112] However, a certain amount of water is apparently necessary to suppress the reversibility of the reaction even in fairly strong aprotic solvents, because water serves as a "trap" for the carbanion. Thus the rate of decarboxylation of potassium triphenylacetate in THF proved to be a maximum after the addition of 1–3 moles of H_2O per mole of the substrate. At higher concentrations of water, the rate of reaction falls, whilst at lower concentrations the decarboxylation ceases altogether (more precisely the degree of reaction is determined by the concentration of water):[113]

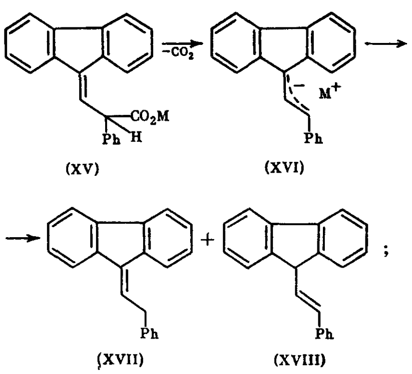
$$Ph_3CCO_2K.\text{crown ether} \rightleftarrows K^+.\text{crown ether} + Ph_3CCO_2^- \xrightarrow[-CO_2]{} Ph_3C^- \xrightarrow{H_2O} Ph_3CH.$$

An especially marked increase of the rate of decarboxylation has been observed in aprotic dipolar solvents, for example, the rate of decarboxylation of the anion of 3-carboxy-6-nitrobenzoisoxazole (XIV) increases by a factor of 10^5 in DMSO or benzonitrile and by a factor of 10^6 in HMP compared with water:[114–116]



(XIV)

An exceptionally great role of the solvent has been noted also in the decarboxylation of the 3-(fluoren-9-ylidene)-2-phenylproprionate anion (XV):[117]



(XV) (XVI)

(XVII) (XVIII)

M = H (a), Na (b).

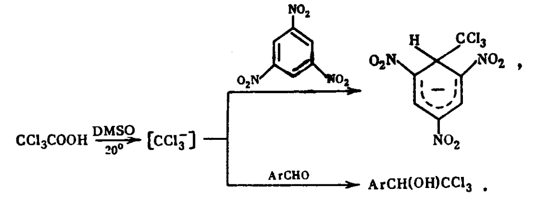
It is of interest that the dissolution of the acid (XVa) in DMSO leads to the instantaneous and quantitative formation of the products (XVII) and (XVIII). On the other hand, the addition of toluene-*p*-sulphonic acid fully suppresses the decarboxylation, which demonstrates yet again that the acid (XVa) is decarboxylated via the anion (XVI).[117]

The addition of crown ethers acts in the same direction as aprotic dipolar solvents.[113,117] It is believed that the main role of crown ethers consists in increasing the solubility of the salts in THF or dioxan, although, apart from this, the formation of complexes with the crown ether apparently increases the resistivity of RCOOM.[113,117]

The influence of the structure of the substituent (R = 9-phenylfluorenyl, fluorenyl, phenylethynyl, triphenylmethyl, and diphenylmethyl) on the rate of decarboxylation of RCOOM in THF or dioxan in the presence of 18-crown-6 ether has been investigated[113] and it has been shown that there is a correlation between the rate of reaction and the pK_a of the CH acids formed during the reaction. Sodium 9-phenylfluorene-9-carboxylate, which forms the most stable carbanion (for the substituents R investigated) (pK_a = 17.9 for 9-phenylfluorene), is decarboxylated at the highest rate, while sodium diphenylacetate, to which corresponds the diphenylmethylanion whose stability is fairly low (pK_a = 32 for Ph_2CH_2), is decarboxylated at the lowest rate.[113] In the presence of 18-crown-6 ether, the rate of decarboxylation increases by a factor of 13–500 depending on the structure.

The extremely marked dependence of the rate of decarboxylation on the nature of the solvent and the added crown ethers undoubtedly indicates the important role of the ions and ion pairs in this process. This is also indicated by data concerning the influence of the counterion. The rate of decarboxylation of triphenylacetates Ph_3CCOOM in THF diminshes in the sequence K > Na > Li. In the presence of 18-crown-6 ether, the rate of reaction increases approximately by a factor of 100.[113] In the decarboxylation of trichloroacetate salts in ethanol, the tetra-alkylammonium salts decompose fastest.[106]

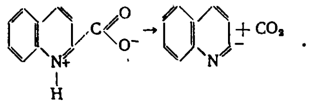
The decarboxylation of acids or their salts in aprotic solvents has long been used to obtain carbanions. Thus trichloroacetic acid in DMSO proved to be the best source of the CCl_3^- anion, because the latter is fairly stable# in this system and can be used in various syntheses:[118-120]



The decarboxylation of 4-nitro-, 2,4-dinitro-, and 2,4,6-trinitro-phenylacetates in DMSO, THF, or DME has been proposed for the generation of nitrobenzyl carbanions, which are difficult to obtain by other methods. The reactions in THF or DME are accelerated by crown ethers.[121]

2. Decarboxylation of Heterocyclic Acids

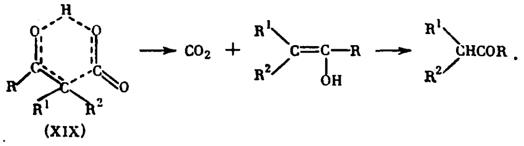
It has been suggested that heterocyclic acids—picolinic, quinaldinic, isoquinaldinic, pyridine-4-acetic, etc. acid—are decarboxylated via zwitter-ions:[97]



Indeed, these acids are stable in highly basic or acid solutions but decompose in neutral solutions.

3. Decarboxylation of β-Ketoacids or β-Dicarboxylic Acids

The decarboxylation of β-ketoacids and β-dicarboxylic acids differs from the decarboxylation of acids with other electron-accepting groups (see above) by certain features. In such cases, both the anions and the undissocated acids are decarboxylated in water and aqueous solutions, the undissociated acids being cleaved more rapidly than the ionised forms.[97,122-125] For example, acetoacetic acid is decarboxylated approximately 50 times faster and malonic acid approximately 10 times faster than the corresponding anion.[97,122-125] The dianions of malonic and phenylmalonic acids are stable in aqueous media.[125,126] It is believed that the decarboxylation of such keto-acids or dicarboxylic acids proceeds via a six-membered transition state of type (XIX) [97,111,122-124,127-129] with the intermediate formation of the enolic forms of the ketones or acids:[97,111]



(XIX)

It is of interest that in the case of dibromomalonic acid the monoanion is decarboxylated incomparably faster than the undissociated acid.[126] Phenylmalonic acid occupies an intermediate position—the rate of cleavage of its monoanion is approximately 5 times higher than the rate of cleavage of the undissociated acid.[126] The monoanions of oxalylacetic acid are also decarboxylated faster, whilst the dianions are stable, as for malonic acid.[130-132]

It is noteworthy that at present there are virtually no data on the decarboxylation of β-ketoacids or β-dicarboxylic acids in anionic forms. There has been only one study in which the influence of the cation and crown ether on the decarboxylation of the acid (XX) and (XXI) was investigated and

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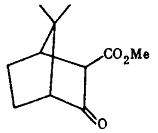
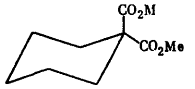
The CCl_3^- anion, formed, for example, on treating chloroform with a base, decompses fairly rapidly with elimination of Cl^-, affording dichlorocarbene.

it was shown that the same tendency is observed for these acids as for triphenylacetic acid.



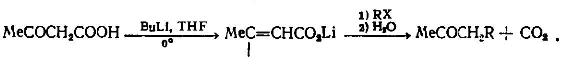
(XX)



(XXI)

The potassium salt is decarboxylated faster in dioxan than the sodium salt and the reaction is accelerated by 18-crown-6 ether.[133] In the decarboxylation of benzoylacetate anions, a fairly marked influence of the substituents was noted, in contrast to the decarboxylation of the undissociated acids.[101,124]

It has been suggested that the lithium enolate of acetoacetic acid be used for the synthesis of ketones:[134]

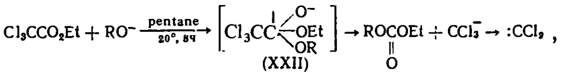


$$\mathrm{MeCOCH_2COOH} \xrightarrow[0^\circ]{\mathrm{BuLi,\ THF}} \mathrm{MeC{=}CHCO_2Li}\ (\mathrm{OLi}) \xrightarrow{1)\,\mathrm{RX}\ 2)\,\mathrm{H_2O}} \mathrm{MeCOCH_2R} + \mathrm{CO_2}\,.$$

The decarboxylation proceeds smoothly at 0 °C.

4. Dealkoxycarbonylation of Carboxylic Acid Esters

Carboxylic acid esters can be cleaved by strong bases (the dealkoxycarbonylation reaction) as happens with carbonyl compounds. Thus ethyl trichloroacetate is cleaved by sodium alkoxides:[135]

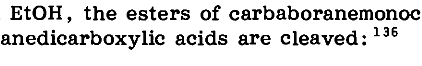


$$\mathrm{Cl_3CCO_2Et} + \mathrm{RO^-} \xrightarrow[20^\circ,\ 8\text{ч}]{\text{pentane}} \left[\mathrm{Cl_3C\overset{|}{C}(O^-)(OEt)(OR)}\right] \rightarrow \mathrm{ROC(=O)OEt} + \mathrm{CCl_3^-} \rightarrow \mathrm{:CCl_2}\,,$$

(XXII)

R = Me, t-Bu.

The intermediate formation of the adducts (XXII) has been unambiguously demonstrated by the isolation of dialkyl carbonates (73–94%). On treatment with catalytic amounts of EtONa and EtOH, the esters of carbaboranemonocarboxylic and carbaboranedicarboxylic acids are cleaved:[136]

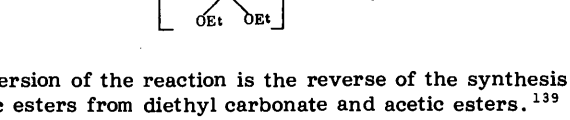


$$\mathrm{H{-}C{-}C{-}COOEt}\ (\mathrm{B_{10}H_{10}}) \xrightarrow[\mathrm{EtOH}]{\mathrm{EtONa}} \mathrm{HC{-}CH}\ (\mathrm{B_{10}H_{10}}) + \mathrm{CO(OEt)_2}\,.$$

We may note that the amides of methyl- and phenyl-barenic acids are just as readily cleaved by H_2NNa in liquid NH_3.[137]

Malonic esters can be cleaved with sodium ethoxide in certain cases, although as a rule this requires high temperatures.[4,138] The cleavage of the diphenylmalonic ester with EtONa in EtOH results in the quantitative formation of diethyl carbonate and the enolate of diphenylacetic ester§ (Scheme 10):[138]

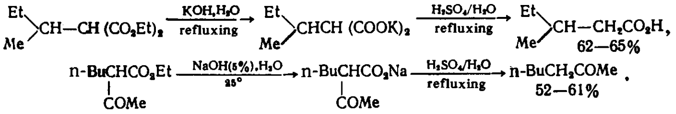
Scheme 10



This version of the reaction is the reverse of the synthesis of malonic esters from diethyl carbonate and acetic esters.[139]

The equilibrium is displaced by distilling of diethyl carbonate. However, in contrast to the cleavage of carbonyl compounds by alkali or alkoxides, this reaction involving esters is not so well known and has not found extensive applications. In many cases it appears as a side reaction, for example, in the acid cleavage of β-ketoesters (see Section II) and in all cases where malonic or cyanoacetic esters have to be heated for a long time with alcoholic alkoxides.[4]

The decarboxylation of β-ketoacid or *gem*-dicarboxylic acid esters is widely used in the synthesis of ketones and monocarboxylic acids. The hydrolysis is usually carried out with acids or dilute alkalis using so far as possible an insignificant excess of the latter in order to avoid the side reaction involving the acid cleavage in the case of ketoesters. Examples are presented below:[4]



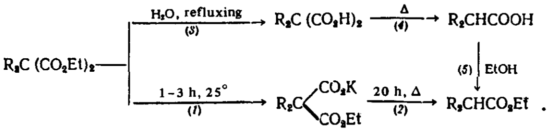
$$\mathrm{Et(Me)CH{-}CH(CO_2Et)_2} \xrightarrow[\text{refluxing}]{\mathrm{KOH,H_2O}} \mathrm{Et(Me)CHCH(COOK)_2} \xrightarrow[\text{refluxing}]{\mathrm{H_2SO_4/H_2O}} \mathrm{Et(Me)CH{-}CH_2CO_2H}\,,\ 62\text{–}65\%$$

$$\text{n-}\mathrm{BuCH(COMe)CO_2Et} \xrightarrow[25^\circ]{\mathrm{NaOH(5\%),H_2O}} \text{n-}\mathrm{BuCH(COMe)CO_2Na} \xrightarrow[\text{refluxing}]{\mathrm{H_2SO_4/H_2O}} \text{n-}\mathrm{BuCH_2COMe}\,.\ 52\text{–}61\%$$

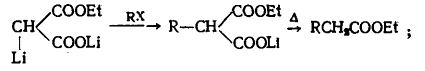
Thus the problem reduces to obtaining acids or their anions, which are then subjected to thermal decarboxylation (already described above).

A method has been proposed recently for the decarboxylation of dicarboxylic acids involving the selective hydrolysis of the diester to the monoester and its decarboxylation in the presence of 18-crown-6 ether [the KOH/crown ether/benzene/ /dioxan/ethanol system (5%)].[133] Since acid esters and not the acids themselves are used in the synthesis, this method is a convenient single-stage alternative to the traditional three-stage synthesis of esters [stages (3)–(5) in Scheme 11]:[133]

Scheme 11



Enolisation may take place as a side reaction, which has already been observed for phenylmalonic esters; nitromalonic ester enolises wholly under these conditions. In this system, it has been possible to carry out the dealkoxycarbonylation of certain ketoesters.[133] Another procedure involves the synthesis of acid esters by alkylating or acylating the dilithio-derivative of monoethyl malonate with subsequent decarboxylation:[140,141]



$$\mathrm{CH(Li)(COOEt)(COOLi)} \xrightarrow{\mathrm{RX}} \mathrm{R{-}CH(COOEt)(COOLi)} \xrightarrow{\Delta} \mathrm{RCH_2COOEt}\,;$$

R=Alk, Ac.

Yet another method has been vigorously developed recently—the decarboxylation of β-ketoesters, malonates, α-cyanoesters, etc. in aprotic dipolar solvents in the presence of small amounts of added water (1–2 moles per mole of the substrate) and salts such as NaCN, NaCl, NaBr, NaI CaI_2, and LiCl (possibly even in catalytic amounts) as 140–180 °C.[98,99,142–147] This method, which had been used earlier to convert monocarboxylic esters into acids (a reaction of the S_N2 type),[148,149] proved to be convenient in many instances for the decarboxylation of substrates sensitive to attack by alkalis or acids. In many cases the best results have been achieved by employing $Me_4NOCOMe$ in DMSO (130 °C) or in HMP (100 °C).[150–152] The *p*-aminothiophenol–Cs_2CO_3–DMF system (130 °C) is probably still more effective, making it possible to eliminate immediately two methoxycarbonyl groups from a single molecule.[153]

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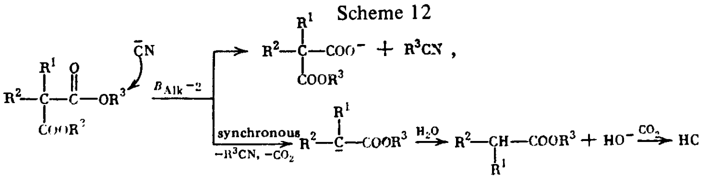
§ When dialkylmalonates are cleaved by EtONa, another pathway predominates: $R_2C(COOEt)_2 + EtONa \rightarrow R_2CHCOOEt + CO + CO_2 + C_2H_6$, etc.; α-vinyl, α-ethyl-, and phenylethylmalonic esters, which are cleaved simultaneously via both pathways, constitute an intermediate case.[138]

It has been suggested that moist DMSO be used in the dealkoxycarbonylation of reactive substrates such as $NCCH_2.COOEt$, $PhCH(COOEt)_2$, 2-ethoxycarbonylcyclopentanone, etc.;[145–147] the cleavage can also be carried out in dry DMSO, but the addition of water lowers the reaction temperature.[146,147] For less reactive substrates, it is essential to add water and frequently also a salt. The greatest effect is produced by NaCN.[144–146]

It is assumed that, in the absence of a salt, the ester is hydrolysed in moist DMSO by the $B_{AC}2$ route. In the KCN–DMSO mixture, the reaction pathway depends on the substrate. Thus in the case of dimethyldiethylmalonate, the formation of MeCN indicates that the $B_{Alk}2$ mechanism of the cleavage reaction predominates[98] (Scheme 12):

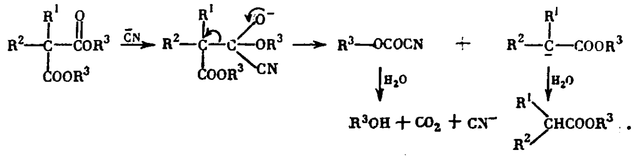
Scheme 12



This scheme is probably valid for other salts MX and for other substrates such as β-ketoesters and α-cyanoesters.[98]

The $B_{AC}2$ mechanism should be preferred for reactions of monosubstituted malonic esters when the process is catalytic (Scheme 13):

Scheme 13

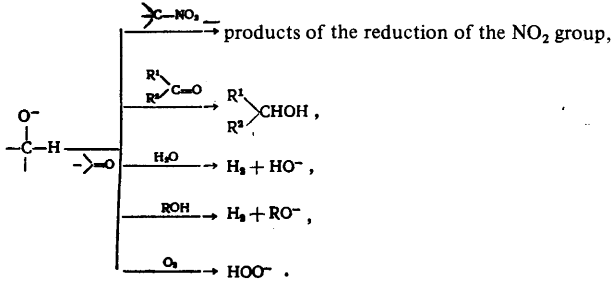


The intermediate formation of carbanions in these reactions can not only be readily demonstrated (by stereoselectivity data and by obtaining α-deuteriated esters and ketones), but can also be used in synthesis. For example, the cleavage of β-ketoesters, α-cyanoesters, or malonates in anhydrous DMSO in the presence of LiCl makes it possible to obtain α-alkylated ketones, acids, and nitriles. Dealkoxycarbonylation in the presence of PhSSPh in HMP affords α-phenylthioketones or α-phenylthioesters.[99] Numerous examples of the synthetic application of the method are quoted in Krapcho's review.[98,99] It has also been suggested that a non-ionic base—1,4-diazabicyclo[2.2.2]octane in xylene—be used for the decarboxycarbonylation of β-ketoesters; the yields of ketones are 84–90%.[154]

IV. THE CLEAVAGE OF ALKOXIDES

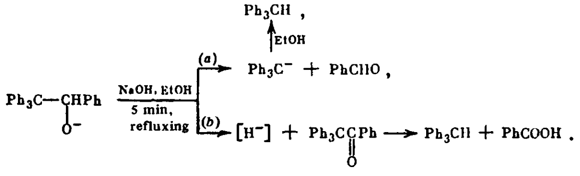
The alkoxides derived from primary and secondary alcohols are known to be potential sources of the hydride ion, which they can transfer to suitable acceptors such as carbonyl compounds, olefins, nitro-compounds, alcohols, etc.[155] (Scheme 14):

Scheme 14

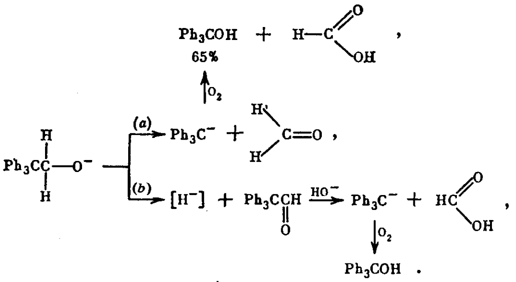


It is assumed that water behaves as the hydride ion acceptor in the dehydrogenation of primary aliphatic and aliphatic-aromatic alcohols by heating with caustic alkalis in aqueous solutions as 200—300 °C (the Dumas–Stass reaction[156]).[157] An alcohol molecule can also serve as the acceptor (200–225 °C).[158,159] In all these reactions (see Scheme 14) a C–H bond is ruptured and they are usually regarded as dehydrogenation or oxidation of alcohols. However, in this Section we shall be interested only in reactions in which C–C bonds are dissociated. This pathway occurs fairly rarely for alkoxides derived from primary or secondary alcohols and requires the presence in the latter of a group R which gives rise to a sufficiently stable carbanion. An example may be provided by the cleavage of phenyltritylcarbinol in an alcoholic solution of NaOH with formation of a mixture of triphenylmethane and benzaldehyde (65% of each) [pathway (*a*), Scheme 15].[160] In principle, the second pathway (*b*) is also possible, because the stabilities of Ph_3C^- and H^- are comparable,[161] but in this case this does not occur (Scheme 15):

Scheme 15

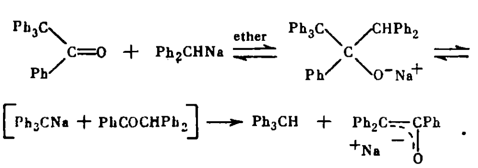


1-Aryl-2,2,2-trichloro- and 1-aryl-2,2,2-tribromo-ethanols are cleaved even more readily.[162] Alcohols of the carbaborane series likewise tend to be cleaved in an alkaline medium.[81] Even a primary alcohol containing the trityl group, namely 2,2,2-triphenylethanol (DME, KOH–O_2), is easily cleaved in an alkaline medium:[163]

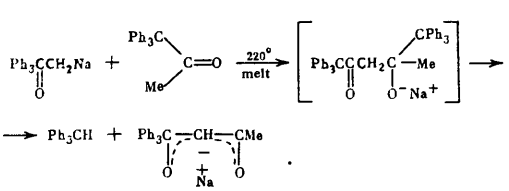


Here it is impossible to make an unambiguous choice between pathways (*a*) and (*b*), since the compositions of the products are identical.

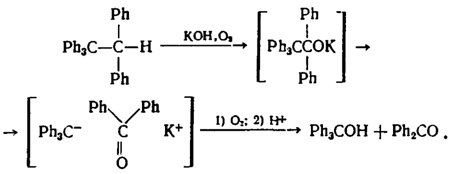
Tertiary alcohols have the greatest tendency to be cleaved, the reaction involving only the rupture of a C–C bond in such compounds. As will be seen below, the ease of cleavage of alkoxides is determined by three most important factors: (1) the presence in the alkoxide RR^1R^2COM of a group to which corresponds a stable carbanion; (2) the bulk of the groups R, R^1, and R^2, because steric compression is eliminated in the transition state of this reaction; (3) the nature of the counterion giving rise to a fairly stable carbanion, in order to achieve their cleavage the introduction into the reaction mixture of trapping agents for the carbanion has been frequently resorted to. The trapping agent is the proton and the cleavage is therefore usually carried out in the presence of water or alcohol. Sometimes the carbonyl compound formed can serve as the source of the proton in the decomposition of alkoxides if it is capable of enolisation. Thus, when an attempt was made to obtain a tertiary alcohol from benzopinacolone and the sodio-derivative of diphenylmethanol, the spontaneous decomposition of the resulting carbinolate was observed:[164]



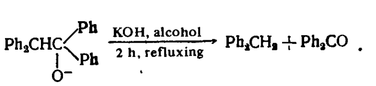
Because of the possibility of the ready elimination of the trityl anion, it has been possible to achieve an unusual Claisen-type condensation of methyl trityl ketone, where the leaving group is, however, the trityl anion:[165]



The alkoxides derived from pentaphenylethanol are apparently also unstable. At any rate, all attempts to obtain pentaphenylethanol by the reaction of Ph_2CO with Ph_3CM (M = Li, Na, or MgBr) proved unsuccessful.[166,167] The extreme instability of this alkoxide is probably to be explained by the steric strain in the molecule combined with the presence of the Ph_3C group, which gives rise to a fairly stable carbanion. This view is confirmed by the results of the oxidation of pentaphenylethane in an alkaline medium.[163] The reaction products in the THF(DME)–KOH–18-crown-6 ether system are triphenylmethanol and benzophenone. Evidently, the alkoxide formed in the reaction is unstable and decomposes to Ph_2CO and Ph_3C^-:[163]



Under mild conditions, the diphenylmethyl anion is split off:[168,169]



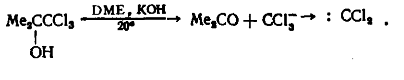
$$\text{Ph}_2\text{CHC(Ph)}_2\text{O}^- \xrightarrow[\text{2 h, refluxing}]{\text{KOH, alcohol}} \text{Ph}_2\text{CH}_2 + \text{Ph}_2\text{CO}\ .$$

In aqueous alcoholic solutions in the presence of KOH, tertiary alcohols containing the CCl_3 group are readily cleaved:[170,171]

$$(p\text{-XC}_6\text{H}_4)_2\text{C(OH)CCl}_3 \rightarrow (p\text{-XC}_6\text{H}_4)_2\text{C(O}^-\text{K}^+)\text{CCl}_3 \rightarrow (p\text{-XC}_3\text{H}_4)_2\text{CO} + \text{CCl}_3\text{H}\ ,$$
X=H, Cl.

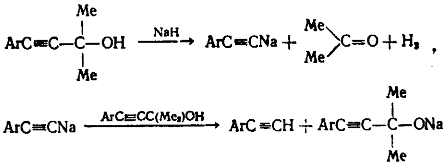
It has been shown that the rate of reaction increases linearly with increase of the concentration of the base.

When dimethyl(trichloromethyl)methanol was maintained in the DME–KOH system in the presence of cyclohexene, dichloronorcarane was obtained,[163] which is associated with the formation of $:CCl_3$ from the trichloromethyl anion:

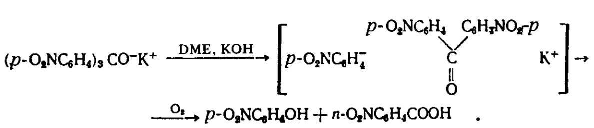


$$\text{Me}_2\text{C(OH)CCl}_3 \xrightarrow[20^\circ]{\text{DME, KOH}} \text{Me}_2\text{CO} + \text{CCl}_3^- \rightarrow :\text{CCl}_2\ .$$

Acetylenic alcohols[172–175] and β-nitroalcohols[176] are fairly readily cleaved. It has been suggested that Ag_2CO_3 on celites in toluene,[174] Ag_2CO_3 and Ag_2O in DMSO (20 °C),[175] or K_2CO_3 at 150–160 °C [173] be used for the cleavage of acetylenic alcohols. Such cleavage can sometimes be conveniently used for the synthesis of arylacetylenes:[177,178]

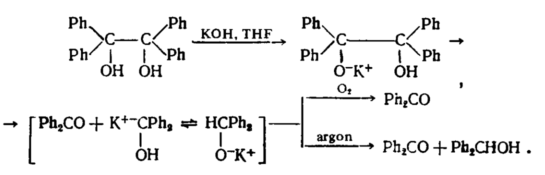


In the examples enumerated above, the proton usually serves as the "trap" for carbanions. Oxygen can sometimes be conveniently used as such a "trap".[20,163] Thus tris(p-nitrophenyl)methanol is readily cleaved in the DME–$KOH–O_2$ system, forming p-nitrophenol and p-nitrobenzoic acid.[20,163,179] We may note that, in the cleavage of alcohols as well as carbonyl compounds (see Section II), the attack by the electrophile or oxidant may be directed to a polarised C–C bond or ion pair and not to the free carbanion R^-:

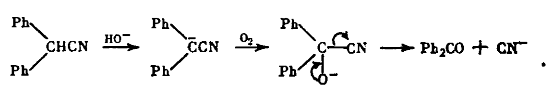


In the absence of O_2, a mixture of products which is difficult to separate, including the products of the reduction of the NO_2 group is formed. Lithium carbinolate is stable under these conditions. Triphenylmethanol is recovered unchanged even after heating for 48 h at 60–70 °C in the KOH–HMP–O_2 system, but the introduction of even one NO_2 group in the *para*-position in the benzene ring is sufficient for the rapid cleavage of the carbinolate (DME–KOH–O_2) with formation of p-nitrophenol and benzophenone. Even benzyldiphenylmethanol is cleaved in this system (60–70 °C, yield of PhCOOH 70–75%). The stability of the benzyl anion ($pK_a = 35$ for PhMe [31]) is apparently critical for the given conditions,[163] because the phenyl anion is not split off.

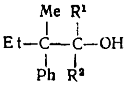
Aromatic ditertiary alcohols, for example, benzopinacol, are extremely readily cleaved:[163]



From the standpoint of the stability of alkoxides, the ready decomposition of cyanohydrins into the initial components in an alkaline medium can be readily understood, because the stable cyanide anion is split off.[180,181] This reaction apparently constitutes the basis of the oxidative decyanation of secondary nitriles in an alkaline medium:[182–184]



In the examples quoted above, the tendency of alcohols to be cleaved was determined mainly by the stability of the carbanion formed, although one cannot fully rule out also the influence of steric factors. This influence becomes of primary importance in the cleavage of tertiary alcohols of the benzyl type,[77,78] i.e.



$$\mathrm{Et{-}C(Me)(Ph){-}C(R^1)(R^2){-}OH}$$

The rate of cleavage of these alcohols varies within wide limits as a function of the experimental conditions—the nature of the solvent and the base, etc. However, in general the ease of cleavage increases gradually in the following sequence of R^1R^2 groups: Ph_2 < PhMe < EtMe < Me_2, which corresponds overall to a gradual decrease in the size of the leaving group. This fact led to the conclusion that the weakening of the steric compression is one of the driving forces in anionic cleavages of this kind.[77,78] We may note that, in the given instances, a fairly stable carbanion is nevertheless formed.

Under more severe conditions (200–300 °C), the alkoxides derived from purely aliphatic tertiary alcohols are cleaved, the rate of cleavage being higher the greater the degree of branching.[185] Triethylmethanol is not cleaved even on heating to 335 °C in the presence of $NaNH_2$, but sodium di-t-butylneopentylmethoxide is cleaved when an attempt is made to obtain it from the corresponding carbinol and NaH:[185]

$$\mathrm{(Me_3C)_2\,(Me_3CCH_2)COH \xrightarrow{NaH} (Me_3C)_2\,(Me_3CCH_3)\,CO^-Na^+ \rightarrow}$$
$$\mathrm{\rightarrow (Me_3C)_2\,CO + Me_3CCOCH_2CMe_3 + Me_2C{=}CH_2 + Me_4C\ .}$$

The carbanionic character of the cleavage of these alcohols, which do not give rise to stable carbanions, is emphasised by the just as marked influence of the counterion as that noted for alcohols capable of splitting off fairly stable carbanions R^-: Li > K > MgX [185] (see below). The successful use of organolithium compounds, in contrast to RMgX, for the synthesis of branched alcohols can apparently be accounted for precisely by the stability of the alkoxides,[186,187] Thus diisopropylneopentylmethanol is formed in 70% yield by the reaction of iso-Pr_2CO with neopentyl-lithium,[185] but the yield is only 4% in the reaction with neopentylmagnesium chloride.[188]

The influence of the solvent is usually very great in reactions with participation of carbanions. The reaction involving the cleavage of alcohols is not exceptional in this sense. Thus, on treatment with dimsylpotassium in DMSO, tri-t-butylmethanol undergoes exothermic cleavage with formation of bi-t-butyl ketone and isobutane:[189]

$$\mathrm{(Me_3C)_3\,COH \xrightarrow{MeSOCH_2^-K^+} (Me_3C)_3\,CO^-K^+ \rightarrow Me_3CCOCMe_3 + [Me_3C^-K^+]\ ,}$$
$$\mathrm{[Me_3C^-K^+] \xrightarrow{MeSOCH_3} Me_3CH + Me_3SOCH_2^-K^+\ .}$$

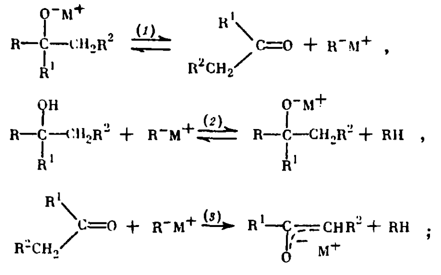
Even more stable alcohols are cleaved in HMP on treatment with BuLi:[190]

$$\mathrm{RR^1R^2COH \xrightarrow{BuLi} RR^1R^2CO^-Li^+ \rightarrow R^1R^2CO + RLi \xrightarrow{H_2O} RH\ .}$$

R, R^1, and R^2 represent different combinations of adamantyl, norbornyl, and 1-bicyclo[2.2.2]octyl and t-butyl groups. We may note that even lithium alkoxides are readily cleaved in this case.

In connection with the possibility of cleaving alkoxides, the question of the reversibility of the reaction involving the addition of organometallic compounds to aldehydes and ketones must inevitably arise. In contrast to other carbonyl compound condensation reactions (for example, the aldol and Claisen condensations), the reversibility of this reaction is not quite so widely known. Apparently, the reaction of RM with ketones as a reversible process was first† considered by Zook et al.[185] Their study of the decomposition of alkoxides derived from tertiary alcohols led them to the conclusion that the process is general for alkoxides with a branched structure and represents the reaction which is the reverse of the addition of RM to ketones (Scheme 16):

Scheme 16

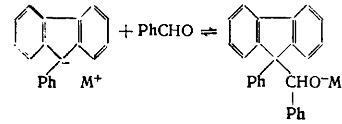


M = alkali metal .

According to the authors, the process can be reversible even when the equilibrium position in stage (*1*) is displaced far to the left, because, in the presence of an excess of the tertiary alcohol or the enolisable ketone, the equilibrium is displaced or is altogether disturbed by the conversion of RM into a hydrocarbon [stages (*2*) and (*3*) in Scheme 16].[185] It is noteworthy that the very possibility of the decomposition of the alkoxide with formation of a ketone and RM is evidence in support of the reversibility of reaction (*1*) in the general case. At the present time convincing evidence has been obtained for the existence of such equilibrium in various systems.

It is known that in aprotic media the stability of alcohols falls significantly compared with protic media.[192] Furthermore, the stability of the alkoxides ROM depends very markedly on the counterion M, diminishing in the sequence Li > Na > K.[193–195] The influence of the counterion on the association constant is manifested particularly strongly in aprotic dipolar solvents. Thus in DMSO the ionic association constants for t-BuOK are 10^8, 10^6, 270, and 200 litre mol^{-1} for M = Li, Na, K, and Cs respectively.[194] The equilibrium position (Scheme 16) can therefore vary significantly as a function of the nature of the counterion. Indeed, in the study of the reaction of benzaldehyde and cyclohexanone with fluorenyl and 9-phenylfluorenyl salts it was shown that the equilibrium in ether and DME is displaced wholly to the right for M = Li and Na and wholly to the left for M = Cs (scheme 17):[196,197]

Scheme 17



(XXIII) M=Cs

(XXIV) M=Li, Na

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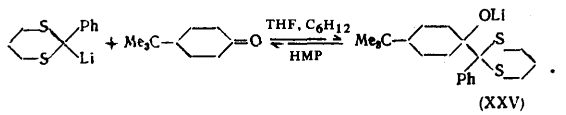
† Some indication of the reversibility of the reaction of RLi with ketones may be found in the paper of Swain and Kent,[191] although in the equation presented only the stage involving the formation of the complex between the carbonyl compound and RLi was reversible.

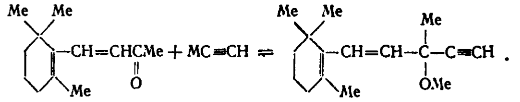
For M = K, it was possible to observe a "living" equilibrium in which both the alkoxide (XXIV) and the initial carbanion (XXIII) are involved. The equilibrium position depends significantly also on the solvent. Thus, if at the end of the reaction with the lithium salt in DME the solvent is replaced by HMP, the reaction equilibrium is fully displaced towards the initial reactants.[196,197]

A similar situation has been observed in the reaction of 2-lithio-2-phenyl-1,3-dithiane with t-butylcyclohexanone:[198]



(XXV)

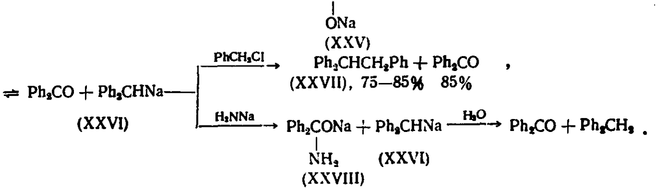
The carbinolate (XXV) is formed in 90% in C_6H_{12} and 75% yield in THF, while in HMP the reaction does not occur. The authors showed that this is associated with the reversibility of the reaction, because the carbinolate (XXV), known to be formed *a priori* in HMP, was converted into the initial compound. The changes in the degree of reaction of α- and β-ionones and benzylideneacetone with metal acetylides can probably be accounted for precisely by the different stabilities of the alkoxides (or, in other works, by the reversibility of the reaction).[199] Thus, in the reaction with β-ionone, the yield of the alcohol is low for M = K, increases to 15–27% for M = Na, and reaches 63–86% for M = Li:



An analogous picture has been observed in the reaction with benzylideneacetone (the yield of the alcohol is 40% for M = K, 71% for M = Li, and 96% for M = Ca) and with β-ionone (30% for M = Na, 67% for M = Li, and 67% for M = Ca).[199] The failure of the attempt to synthesise tertiary alcohols of the carbaborane series from ketones and lithio-derivatives of barenes has been explained[81] by the instability of such alcohols.

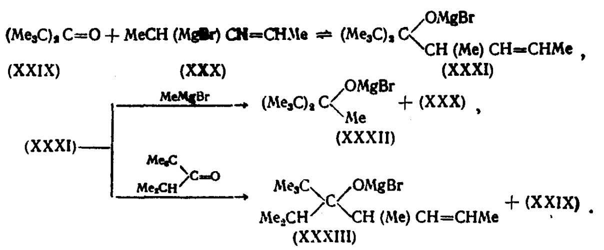
The reversible reactions quoted above involve stable carbanions of the type of fluorenyl or ethynyl carbanions. In the case of less stable carbanions, the reversibility of the reaction can be demonstrated by employing "trapping agents"—a carbonyl compound or RM. The existence of equilibrium in the reaction of benzophenone with diphenylmethylsodium was apparently first demonstrated precisely with the aid of this procedure (Scheme 18):[17,200]

Scheme 18

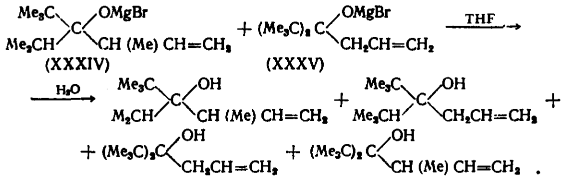


Indeed the addition of benzyl chloride to the reaction mixture leads to the formation of the alkylation product (XXVII), while the introduction of sodium amide results in the isolation of the adduct (XXVIII). The latter reaction is accompanied by the appearance of a red colour due to the carbanion (XXVI).[17]

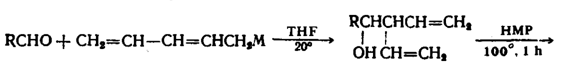
The reversibility of the reaction with ketones has been convincingly demonstrated also for organometallic compounds of the allyl type (M = Li, MgX, or ZnX).[201–214] One of the procedures used for this purpose is similar to that quoted by Hamrick and Hauser.[17] On treatment of the adducts (XXXI) with an excess of RMgX (R = Me or CH_2=CHMe), the tertiary alkoxide (XXXII) was obtained, in which the dimethylallyl group had been replaced by R, while on heating compound (XXXI) with iso-PrCOBu-t, which is more reactive than the ketone (XXIX), the adduct (XXXIII) was isolated together with t-Bu_2CO (XXIX):



In the case of CH_2=CH=CH_2MgX or α- and γ-dimethylallylmagnesium halides, where the initial and rearranged products are identical, the reversibility of the reaction was demonstrated by means of a "cross" reaction—when a mixture of the two carbinolates (XXXIV) and (XXXV) is refluxed, a mixture of four carbinolates is formed evidently as a result of the decomposition of compounds (XXXIV) and (XXXV) into the initial reactants and their subsequent interaction:[206]

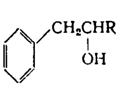


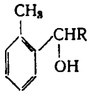
The thermal decomposition of carbinolates of the allyl type has also been carried out.[202,207,215] As was to be expected, the rate of decomposition increases with increase of the bulk of the substituents: t-Bu > iso-Pr ≅ cyclo-C_6H_{11} > Ph > Et.[207] It has been suggested that the reactions of allylic organometallic compounds, containing a strained diene system, with ketones and even with aldehydes are also reversible.[218,219] As already reported, the ratios of the products in these reactions depend significantly on their conditions. The strong influence of the nature of the cation M (Li, Na, Zn, and Al) on the mode of reaction has been noted in many communications.[204,215–218] It is therefore evident that the reversibility of such reactions can be used for synthesis purposes. Indeed, studies in which alcohols with a specified structure were synthesised by the reaction of such RM with carbonyl compounds have already been published.[215–218] For example, when the aldehydes RCHO are treated with CH_2=CHCH=$CHCH_2$M (M = ZnBr or Li) at the usual temperature, alcohols with a branched structure are formed exclusively, but, with increase of temperature and after the replacement of THF by HMP, the formation of only linear alcohols is observed:[216]

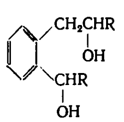


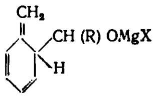
$$\mathrm{RCHO + CH_2{=}CH{-}CH{=}CHCH_2M \xrightarrow[20^\circ]{THF} \underset{OH\ CH=CH_2}{RCHCHCH=CH_2} \xrightarrow[100^\circ,\ 1\ h]{HMP} \underset{OH}{RCHCH_2CH=CHCH=CH_2}}\ .$$

Thus the ability of allylic carbinolates to decompose into the initial ketone and allylmetal has been established. The possibility of the cleavage of magnesium carbinolates with formation of the benzyl Grignard reagent has been comparatively recently demonstrated. Throughout many years, chemists have been interested in the reaction of benzylmagnesium halides with aldehydes, in which the formation of "anomalous" products, namely o-tolylmethanol (XXXVII) [220–225] and the diol (XXXVIII) or its dehydration product,[222–231] was observed together with the formation of the so called "normal" alcohols (XXXVI):


(XXXVI)


(XXXVII)


(XXXVIII)

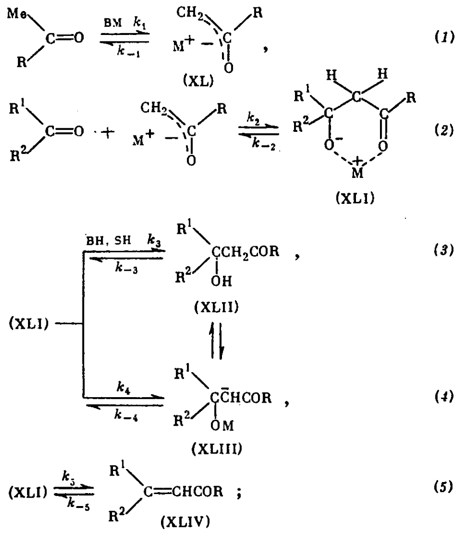

(XXXIX) .

Convincing evidence showing that the diol (XXXVIII) and possibly also the "normal" alcohol (XXXVI) are secondary products, whose formation can be explained by the reversible dissociation of the adduct (XXXIX) arising initially and subsequent reactions, has been obtained only comparatively recently.[232–234]

V. THE RETROALDOL CONDENSATION

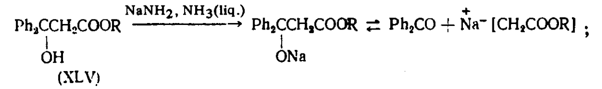
As shown in Section IV, tertiary alcohols containing a group R to which corresponds a sufficiently stable carbanion are cleaved in an alkaline medium, the ease of such cleavage depending primarily on the stability of the carbanion. It is quite evident that the alkoxides derived from β-hydroxycarbonyl compounds (the products of aldol condensation) must be unstable, because their cleavage results in the formation of the enolates of aldehydes, ketones, and esters, i.e. fairly strong CH acids (pK_a = 25–20).[31] Indeed, aldol condensation in an alkaline medium is a reversible process (Scheme 19) and all its stages are reversible:

Scheme 19



a) $R^1 = R^2$ = Alk or Ar
b) R^1 = Alk, Ar; R^2 = H
c) R^1 = Alk, Ar; R^2 = OAlk .

In order to obtain the target products, it is therefore necessary to select special conditions. However, in general, one may say that the condensation is promoted by the use of strong bases in stoichiometric or even larger amounts [in order to shift the equilibrium (*1*) to the right], by the removal of the condensation product from the reaction sphere [for example by its precipitation as the carbinolate (XLI) or the dianion (XLIII)], by a low temperature, and by a short reaction time.[4,92] On the other hand, the retroaldol cleavage will be promoted by the employment of catalytic amounts of bases, by an elevated temperature, by a long reaction time, and by the presence of trapping agents (for example, water or alcohol), which are capable of reacting with the enolates (XL), displacing thereby the equilibrium in stage (*1*) to the left. Indeed, retroaldol cleavage is as a rule carried out in aqueous or alcoholic solutions. In non-aqueous media there is also a possibility of retroaldol decomposition, because the initial reactants are more stable than the condensation products. However, since in non-aqueous media the hydroxycarbonyl compound (XLII) can itself function as a trapping agent for the enolate (XL), in the presence of stoichiometric amounts of bases, whereupon only the carbinolate (XLI) is present in solution, the retroaldol decomposition may not occur. Such a situation has been observed for the β-hydroxyester (XLV), which is cleaved by catalytic amounts of H_2NNa in liquid ammonia, but is not cleaved by the stoichiometric amount of H_2NNa:[235]



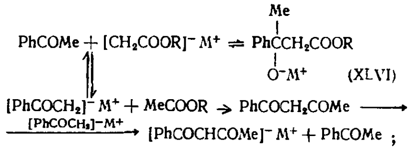
$$\underset{\underset{(XLV)}{OH}}{\mathrm{Ph_2\overset{}{C}CH_2COOR}} \xrightarrow{\mathrm{NaNH_2,\,NH_3(liq.)}} \underset{ONa}{\mathrm{Ph_2CCH_2COOR}} \rightleftarrows \mathrm{Ph_2CO} + \overset{+}{\mathrm{Na}}{}^{-}[\mathrm{CH_2COOR}]\ ;$$

R=Et, iso-Pr, t-Bu.

As an example illustrating the influence of the reaction time on the yield of products, one may quote the condensation of benzophenone with alkyl acetates MeCOOR (R = Et or iso-Pr) in the presence of equimolar (and larger) amounts of H_2NNa in liquid ammonia.[235] For a short reaction time (neutralisation 5 min after the addition of Ph_2CO to the enolate), β-hydroxyesters (XLV) are formed in yields of ~70%, but, following an increase of the reaction time to 1 h, only the initial reactants are recovered.

Yet another procedure which is resorted to in order to shift the equilibria in aldol condensations involves the selection of the corresponding cations M^+. The dependence on the nature of the cation is the most interesting feature of these reactions. Thus acetophenone readily condenses in liquid ammonia with the enolates of alkyl acetates $[CH_2COOR]M^+$, where M = Li or ZnCl, but the adducts are not formed under these conditions with the Na enolates. Comparison of the alkoxides (XLVI), know to have been obtained *a priori*, showed that the lithium alkoxides are much more stable than the sodium or potassium alkoxides. Indeed, the sodium salt (XLVI) decomposes on refluxing in ether for 2 h, while the lithium or ZnCl salts are cleaved only on refluxing in toluene or dibutyl ether[235,236] (Scheme 20):

Scheme 20

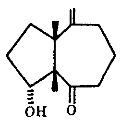


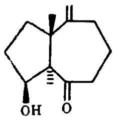
$$\mathrm{PhCOMe} + [\mathrm{CH_2COOR}]^- M^+ \rightleftharpoons \underset{O^-M^+}{\overset{Me}{\mathrm{Ph\overset{|}{C}CH_2COOR}}}\quad (XLVI)$$

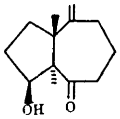
$$[\mathrm{PhCOCH_2}]^- M^+ + \mathrm{MeCOOR} \rightarrow \mathrm{PhCOCH_2COMe} \longrightarrow \xrightarrow{[\mathrm{PhCOCH_2}]^- M^+} [\mathrm{PhCOCHCOMe}]^- M^+ + \mathrm{PhCOMe}\ ;$$

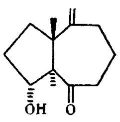
M=Li, Na, K, ZnCl .

We may note that the decomposition of compound (XLVI) can lead not only to the initial reactants but also to products of other condensations, for example, to benzoylacetone and acetophenone, which are formed as a result of the transmetallation and subsequent Claisen acylation. A similar influence of the cation M^+ has been noted also for the adducts (XLV).[235] In the series of the usual alcohols ROH, the dependence of the stability of the alkoxides on the nature of the counterion is well known (see Section III). In the case of β-hydroxycarbonyl compounds, the dependence of the stability of the enolate on the nature of the metal is determined not only by the strength of the O–M bond but also by the ability of the carbonyl group to form chelates, which promotes a shift of the equilibrium in the second stage of the condensation to the right (see Scheme 19). The ability of a definite series of metals (Li, Zn, B, etc.) to form stable chelates is widely used to achieve high regio- and stereoselectivities of aldol condensations.[4,237,238] Consequently, it is best to employ potassium or sodium as the cation for the retroaldol reaction. An interesting application of the retroaldol–aldol condensation sequence has been proposed[239] for the synthesis of isomeric perhydroazulene hydroxyketones (XLVII)–(L). Depending on M^+ in the base (Li, Na, or K) and the reaction time, it is possible to obtain predominantly the isomers (XLIX) or (L) or an equilibrium mixture of all four isomers from the isomers (XLVII) and (XLVIII).[239]


(XLVII)

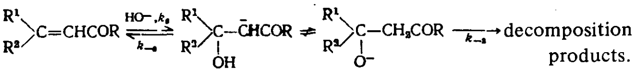

(XLVIII)


(XLIX)


(L)

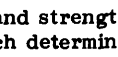
Thus, when (iso-Pr)$_2$NLi was used in THF, the selective conversion of the isomer (XLVII) into (XLIX) and of (XLVIII) into (L) was observed. The stereoselective course of the reaction was promoted by the low temperature and the short reaction time. For example, when the isomer (XLVII) is treated with (iso-Pr)$_2$NLi for 5 min (THF, 20 °C), then the isomer (XLIX) is formed in 65% yield, but, when the reaction mixture is kept for 45 min, almost equal amounts of the isomers (XLIX) and (L) are isolated. When the isomer (XLVII) or (XLVIII) is treated with a methanol solution of NaOH, virtually identical mixtures of all four isomers are formed, i.e. equilibrium is established in the system.[239]

Kinetic study of the decomposition of β-hydroxyketones (ketols) in an alkaline medium showed that ketols undergo two competing reactions—decomposition into the initial carbonyl compounds and dehydration.[204–205] Dehydration (crotonic condensation, Claisen–Schmidt condensation) is the reaction by means of which it is sometimes possible to displace the equilibria in such reactions towards the formation of the products. However, enones can also be unstable in alkaline media; by combining with the hydroxide anion via the Michael reaction, they are reconverted into the ketols and further into cleavage products, the ketol being present in such cases at a stationary concentration. Under certain conditions, it is possible to observe also an equilibrium mixture of all the components:[240–245]

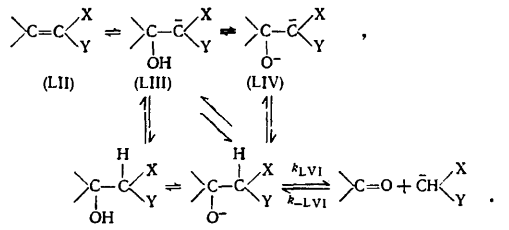


(XLIV) (LI) (XLI)

Each of the processes—dehydration and cleavage of the ketols into the initial reactants—is of second order overall and of first order with respect to each reactant (sometimes even higher with respect to the alkali) and the rate-determining stages are usually the reactions on the anions (XLI) and (LI) (k_{-2} and k_{-6}).[240–251]

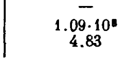
Naturally in an alkaline medium not only enones but also other compounds with an activated double bond are cleaved (for example, the products of the Knoevenagel condensation). It has been established qualitatively that the ease of cleavage of compounds of the type  $R^1R^2C{=}CXY$ (LII) (X and Y are electron-accepting groups and R^1 and R^2 = alkyl or aryl) depends primarily on the number and strength of the electron-accepting groups X and Y, which determines the stability of the carbanions formed. The influence of alkyl and aryl groups is not so great, but alkyl derivatives are as a rule cleaved more readily than aryl derivatives. The presence of electron-accepting groups in the substituents R^1 and R^2 inhibits the reaction, which is in fact understandable, since the "expelling force" of the group R^1R^2CO diminishes.[252–254] However, despite the simple and understandable qualitative pictures, the mechanism of this reaction is fairly complex and depends significantly on the pH of the medium.[256–263] An overall mechanism of the hydrolytic cleavage of activated olefins (Scheme 21) has been proposed on the basis of the analysis of kinetic data for the cleavage of a series of olefins using a flow technique with spectrophotometric recording:[258–263]

Scheme 21



The most general mechanism in basic media involves the addition of the base to the olefin (LII) with formation of the anion (LIII), which is followed by its protonation to compound (LV), the formation of the anion (LVI), and its decomposition into products. In a highly alkaline medium, there is a possibility of another pathway—the formation of the dianion (LIV) and its subsequent protonation to compound (LVI) or intramolecular proton transfer in the anion (LIII) with formation of the anion (LVI). For example, it has been shown that, in the cleavage of 1,1-dinitro-2,2-diphenylethylene in 50% DMSO (H_2O) at pH 13.5, the rate-determining stage is the protonation of the dianion (LIV); at pH 12.5–13.5, the rate is determined by the protonation of compound (LIII) and at pH 11–12 it is determined by the attack by the hydroxide ion with formation of compound (LIII); at pH 10, the slow stage probably involves the attack by water on the substrate (LII).[259] The conversion of compound (LV) into the reaction products (in which the present authors are interested) using the stopped flow technique can be identified as an independent two-stage process,[258–263] the rate-determining stage of which may be also the deprotonation of the adduct (LV), while the rapid stage is the decomposition of compound (LVI) into the products.[258,259,263]

Table 1. Kinetic data for the retrodecomposition of the anion (LVI) and for its formation in water at 25 °C.[261]

Kinetic data	$PhCH{=}C(CN)_2$	$ArCH{=}C(NO_2)_2$*	
k_{LVI}, s^{-1}	$4.66\cdot10^4$	$6\ 32\cdot10^2$	$5\cdot10^8$
k_{-LVI}, litre mol^{-1}	$1.70\cdot10^5$	0.2	—
K, mol $litre^{-1}$	$2.74\cdot10^{-1}$	$3\ 16\cdot10^3$	$1.09\cdot10^8$
pK_a for CH_2X_2	11.19	10.2	4.83

---

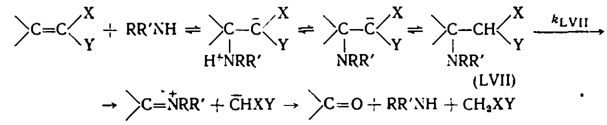
*Ar = 3,4-methylenedioxyphenyl.[257]

However, on comparing the rate constants for the decomposition of the anion (LVI) into the products, it was found that, for the olefins investigated, there is no correlation between these rates and the pK_a of the corresponding hydrocarbons (Table 1). Dicyanomethane is a weaker CH acid than dinitromethane, while the rate of abstraction of the dicyanomethyl anion from the adduct (LVI) is higher almost by two orders of magnitude than the rate of abstraction of $\bar{C}H(NO_2)_2$.[261] The causes of this are so far not understood. Table 1 also lists the rate constants k_{-LVI} for the condensation stage and the equilibrium constants.

An analogous picture has been observed in the hydrolytic cleavage of activated olefins by amines.[264] It has been shown that an adduct of type (LVII) is formed as an intermediate in this process and subsequently decomposes into the product [264–267] (Scheme 22).

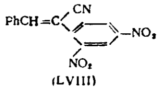
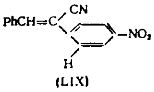
Comparison of the rates of cleavage of several such adducts showed that in this case there is no correlation between the rate of cleavage and the pK_a of the hydrocarbon CH_2XY. Thus, as was to be expected, the adduct of the olefin (LVIII) is cleaved faster than the adduct of the olefin (LIX) but more slowly than the adducts of benzylidenemalonitrile, although, judging from the pK_a of the hydrocarbon CH_2XY, the opposite sequence should have been obtained (Table 2).

Scheme 22

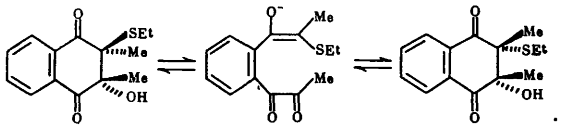


$$\rangle C{=}C\langle^{X}_{Y} + RR'NH \rightleftharpoons \rangle\underset{H^{+}NRR'}{C}{-}\bar{C}\langle^{X}_{Y} \rightleftharpoons \rangle\underset{NRR'}{C}{-}\bar{C}\langle^{X}_{Y} \rightleftharpoons \underset{(LVII)}{\rangle\underset{NRR'}{C}{-}CH\langle^{X}_{Y}} \xrightarrow{k_{LVII}} \rangle C{=}\overset{+}{N}RR' + \bar{C}HXY \rightarrow \rangle C{=}O + RR'NH + CH_2XY$$

Table 2. The rate constants for the decomposition of the adducts (LVII) with piperidine (RR'NH = piperidine).[264]

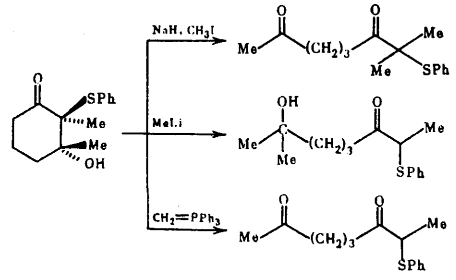
Kinetic data	 (LVIII)	 (LIX)	PhCH=C(CN)$_2$
k_{LVII}, s^{-1}	9.4	4.5·10^{-3}	33
pK_a for CH_2XY	8.06	12.62	10.21

The retroaldol decomposition is frequently an undesirable side reaction, which must be borne in mind in carrying out condensations of the aldol or crotonic type. However, this reaction has also found some applications in synthesis. As an example, one may quote its use for the *cis–trans*-isomerisation of β-hydroxycarbonyl compounds.[268,269] Thus the *trans*-dihydronaphthoquinone derivative (LX) undergoes a base (EtS$^-$ or EtO$^-$)-catalysed rearrangement to the *cis*-isomer (LXI) via a sequence of retroaldol–aldol condensations [and conversely (LXI) → (LX)]:[268,269]



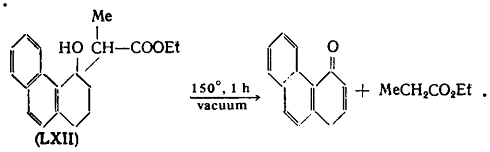
(LX) (LXI)

It has been suggested that the enolates formed in retroaldol processes be made to react with electrophilic trapping agents in order to obtain acyclic compounds with functional groups from cyclic compounds:[270]



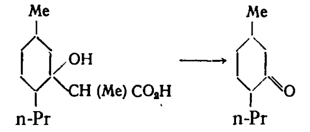
The cleavage of unsaturated acids or nitriles is used to synthesise isotope-labelled acids having two carbon atoms less than in the initial compounds.[271] The cleavage of β-hydrocarbonyl compounds and activated olefins can be usefully employed in all cases where the cleavage products are less readily available than the initial compounds.[91,272]

In conclusion, we may note that cases of ready thermal decomposition of β-hydroxycarbonyl compounds are known. Thus the hydroxyketone (LXII) is cleaved quantitatively into ethyl propionate and 4-oxo-1,2,3,4-tetrahydrophenanthrene at 150 °C:[273]

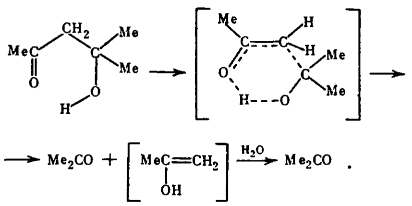


(LXII)

α-Menthylpropionic acid is cleaved on distillation:[274]



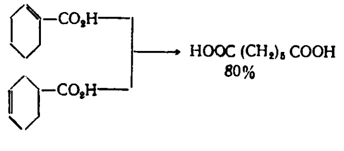
It has been suggested that a six-membered transition state is formed on thermal decomposition in the gas phase or in inert solvents:[275]



The examples listed above do not exhaust the possible types of cleavage of C–C bonds in alkaline media. Fairly numerous complex reactions involving to some extent retrodecomposition (retro-Claisen, retroaldol, etc.) stages, examined above, are known. We shall quote here several such reactions which are of practical importance. For example, the cleavage of unsaturated aliphatic acids constitutes a method of synthesis of saturated acids having two carbon atoms less than the initial acids:[276]

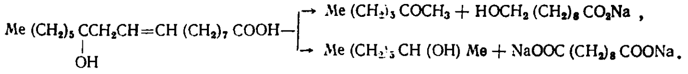
$$Me(CH_2)_7CH{=}CH(CH_2)_7CO_2H \xrightarrow{200-360°} Me(CH_2)_{14}CO_2H + CH_3CO_2H + H_2 \ .$$

By heating cyclohexene-1-carboxylic or cyclohexene-3-carboxylic acid or their nitriles with alkalis in autoclaves at high temperatures (250–350 °C), pimelic acid is obtained:[277–279]



Azelaic acid is obtained in exactly the same way from cyclooctene-1-carboxylic and cyclooctene-4-carboxylic acids.[280] In most such reactions, the mechanism cannot be always readily traced, although it is evident that the unsaturated acids isomerise to αβ-unsaturated acids, combine with water via the Michael reaction, and the resulting hydroxyacids are dehydrogenated to ketoacids, which then undergo the retro-Claisen decomposition.

The cleavage of ricinoleic acid (obtained by hydrolysing castor oil) to sebacic and ω-hydroxydecanoic acids, which has found an application in industry, is even more complex:[281]



$$\mathrm{Me(CH_2)_5\underset{\displaystyle OH}{\underset{|}{C}}H_2CH{=}CH(CH_2)_7COOH} - \begin{cases} \rightarrow \mathrm{Me(CH_2)_5COCH_3 + HOCH_2(CH_2)_8CO_2Na}, \\ \rightarrow \mathrm{Me(CH_2)_5CH(OH)Me + NaOOC(CH_2)_8COONa}. \end{cases}$$

The mechanism of this reaction is unknown.

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Computer-assisted Synthesis

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The state, problems, and prospects of the new field of computer-assisted chemisty, namely the design and search for new ways of synthesising organic compounds with the aid of a computer (computer-assisted synthesis), are described. The principal developments in programming, used directly by organic chemists are examined. The existing programs for computer-assisted synthesis are subjected to a comparative analysis and the features which more than 20 computer systems have in common, including the "FLAMINGOES" system devised by the authors, as well as the differences between them are elucidated. The bibliography includes 123 references.

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I. INTRODUCTION

One of the most important scientific developments involving the application of computers in chemistry is the search for ways of synthesising organic compounds with the aid of a computer, which has come to be referred to in the literature as "computer-assisted synthesis", abbreviated to CS. Since 1969, when the paper of Corey and Wipke,[1] giving a description of the first program for computer-assisted synthesis, was published, this field has developed fairly rapidly and at the present time one may speak of CS not as a set of individual developments but as a major field of science (see, for example, the relevant reviews[2-7]).

The aim of the present review is to cover the principal aspects of the problem of CS. At the same time we have not included in the review the general problems of the strategy and planning of synthesis, because they have already been adequately dealt with in the literature.[8,9] On the contrary, in the present review we shall as far as possible take into account the specific computer-dependent features of the search for methods of synthesis with the aid of a computer. We thought it more useful to differentiate the key factors in the creation of programs for the solution of problems in CS without going into the details of the formulation of algorithms and the machine execution of specific programs, because the number of CS programs is fairly large and is continuously growing. We believe that, within the framework of the selected structure of the description, it will be possible to define clearly the similarities and differences between the existing CS programs and to elucidate the fundamentally new features of a particular approach.

In the concluding part of the review, we shall examine the main principles of the "FLAMINGOES" computer system which we have developed and which can be used, in particular, also for the solution of problems in the planning of synthesis.

It is noteworthy that, like any new field of science, CS has no established universal terminology, which is a significant obstacle to reviewing the relevant data. In the present review, an attempt has been made to present the main aspects of CS in terms of a more unified terminology, which embraces the most apt and accurate, in our view, formulations.

II. FORMULATION OF THE PROBLEM. "THE SYNTHESIS TREE"

Suppose that a certain compound has been specified for which it is necessary to find the possible methods of synthesis from other, precursor compounds. In this case we solve the problem of planning the synthesis in the reverse (retrosynthetic) direction.[1] It is also possible to formulate the opposite problem of the forward (synthetic) planning of the synthesis, i.e. the problem of finding the possible ways in which the given compound or set of compounds reacts and the reaction products.[1] The compound specified (set of compounds) will henceforth be referred to as the chemical system (ChS); as a rule, in the retrosynthetic approach the chemical system includes only one compound while in the direct planning of synthesis there are one or several compounds.

The result of the execution of a CS program in both the forward and reverse directions of the search is the construction of the "synthesis tree", i.e. a graph whose vertices correspond to the initial, intermediate, and final compounds but whose edges represent the chemical reactions in the course of which these compounds are interconverted. If the computer search is carried out in the reverse (retrosynthetic) direction, then the "synthesis tree" is a schematic representation of the possible ways of synthesising the specified chemical system from initial compounds via the intermediate formation of the precursors of the specified chemical system. If the search is carried out in the forward (synthetic) direction, then the "synthesis tree" can be interpreted as the "reactions tree", i.e. as the schematic representation of the possible ways in which the specified chemical system can react.

"The synthesis tree" is constructed as follows in the course of the execution of the CS program. The structure of the compound incorporated in the specified chemical system is introduced into the program. The program generates a set of precursors of the specified chemical system on the basis of empirical or logical instructions inherent in the program. This procedure can be repeated for all or some of the structures generated in the first stage and so on until certain specified conditions governing the completion of the construction of the "synthesis tree" have been fulfilled.

The most important and fundamental factor in CS is the formal treatment and coding of human thought, i.e. without the ideas and reasoning with which the organic chemist operates in selecting or assessing chemical reactions. All the computer systems existing at present for the planning of synthesis constitute only the first and probably fairly tentative steps towards the solution of this fundamental problem. Indeed, so long as a rigorous general theory of organic chemistry has not been created not only an exact prediction of the results of a certain reaction but also the *a priori* assessment of the possibility of the occurrence of this reaction is impossible.[10] Nevertheless, the attempt to reproduce with the aid of the computer all the logical, empirical, and intuitive considerations by which the organic chemist is guided in planning a synthesis appears very useful as a basis for the creation of an artificial intelligence in organic chemistry.

Using the terminology introduced, it is possible to define the task of selecting and assessing the methods of synthesis as one involving the reduction of the "synthesis tree",[11] i.e. the elimination from the latter of chemical reactions and compounds which do not satisfy particular selection criteria. The selection criteria make it possible to diminish greatly the "synthesis tree" and also to organise the generation of the precursor of a given chemical system in such a way that the program generates in the first place the most probable or the most interesting methods of synthesis. The selection criteria are most effective if they operate at the early stages of the construction of the "synthesis tree".

The "synthesis tree" can be constructed under different conditions: (a) non-interactively when the program effects the search, after the input of the necessary initial information, without the interference of the user and without requiring additional information; (b) interactively when the program cannot adopt "independently" a solution in certain situations and turns to the human operator for assistance. Ideally, the CS program should generate the optimum "synthesis tree" without the involvement of the user, but the real situation in theoretical organic chemistry makes it possible to solve under automatic conditions only fairly narrow problems or it requires the introduction into the program of very rigorous limitations, which inevitably leads to the loss of interesting results.

At the present time CS is developing in the direction of increasing the "independence" of programs, although the commonest computer systems provide also for the possibility of an interactive search.

III. PRINCIPAL PROGRAMS FOR COMPUTER ASSISTED SYNTHESIS

As already stated, the aim of the present review is to cover the main aspects of the given scientific field as a whole. The specific features of the tasks to be performed by CS define the main problems on which attention should be concentrated: (a) the representation and analysis of the chemical structure in CS programs; (b) the representation and analysis of chemical reactions (transformations) in CS programs; (c) the selection criteria in CS programs. To facilitate the understanding of the data described below, we quote a brief compilation of the main CS programs with an indication of the leaders of the project, the Company, and the literature references (the most novel computer developments are designated by an asterisk).

"AHMOS"* (Automatisierte Heuristische Modellierung Organisch-chemischer Synthesen); Weise (GDR).[12–15]

"ASSOR" (Allgemeines Simulations-System Organischer Reaktionen); Schubert [Federal Republic of Germany (FRG)].[16,17]

"CAMEO"* (Computer-Assisted Mechanistic Evaluation of Organic Reactions); Jorgensen (USA).[18–26]

"CASP" (Computer-Assistierten Synthese Planung); developed by a Company (FRG, Switzerland).[6]

"CHIRP" (Chemical Engineering Investigation of Reaction Paths); Agnihotri and Motard (USA).[27]

"CICLOPS" (Computers in Chemistry, Logic Oriented Planning of Syntheses); Ugi and Gasteiger (FRG).[28]

"EROS"* (Erzeugung von Reaktionen fur die Organische Synthese); Gasteiger (FRG).[29,30]

"FLAMINGOES"* (Formal-Logical Approach to Molecular Interconversions. Non-empirical Generation, Orientation and Evaluation of Syntheses); Zefirov (USSR).[31–34]

"LHASA"* (Logic and Heuristic Applied to Synthetic Analysis); Corey (USA).[35–41]

"MASSO"; Moreau (France).[42]

"MATCHEM" (MAThematical model of constitutional CHEMistry); Ugi and Gasteiger (FRG).[28]

"OCSS" (Organic Chemical Simulation of Synthesis); Corey and Wipke (USA).[1]

"PASCOP" (Programme d'Assistance a la Synthese des Composes OrganoPhosphores); Kaufmann and Choplin (France).[43–48]

"REACT"; Carhart, Smith, and Djerassi (USA).[49,50]

"REACT" (REACTion path synthesis program for the petrochemical industry); Govind and Powers (USA).[51]

"SECS"* (Simulation and Evaluation of Chemical Synthesis); Wipke (USA).[11]

"SOS" (Simulation of Organic Synthesis); Barone and Chanon (France).[52–54]

"SYNCHEM"* (SYNthetic CHEMistry); Gelernter (USA).[55–58]

"SYNGEN"* (SYNthesis GENeration); Hendrickson (USA).[59–61]

"TOSCA"* (TOpological Synthesis design by Computer Application); Sander (FRG).[62]

Bersohn's program* (Canada).[63–65]

Whitlock's program (USA).[66]

"EPOS"* (Empirical Planning of Organic Synthesis); Koptyug, Smirnov, and Piottukh-Peletskii (USSR).[67]

Many of the programs listed are not fully novel developments, but constitute modifications of programs developed previously, specially designed for the solution of narrower problems than the prototype programs. Thus Whitlock's program and the "SOS" and "PASCOP" systems are based on the same principles as the "LHASA" and "SECS" programs but are designed for the investigation of narrower fields of organic chemistry, such as the synthesis of acyclic structures, the chemistry of heterocyclic compounds, and the chemistry of organophosphorus compounds. The "SECS" program is also the basis of the "CASP" computer system. We shall base the subsequent exposition mainly on novel developments (designated by an asterisk), omitting the non-fundamental modifications of programs and obsolete versions such as "OCSS" (see the newer programs "LHASA" and

"SECS"), "CICLOPS", "MATCHEM" (see the program "EROS"), and "MASSO" (see the program "SYNGEN").

The programs "REACT" and the "CHIRP", "ASSOR", "AHMOS", and "CAMEO" systems occupy a special place among the computer systems enumerated. The program "REACT" (Carhart, Smith, and Djerassi) is an auxiliary component of the "CONGEN" system designed to establish the structure of an unknown compound from spectroscopic and chemical data. The "REACT" system (Govind and Powers) is in many respects similar to the "LHASA" and "EROS" programs but is specially designed for the investigation of chemical engineering processes.

The "AHMOS", "CAMEO", and "ASSOR" programs represent the "mechanistic" tendency in CS. The "AHMOS" and "CAMEO" systems search exclusively in the forward (synthetic) direction generating not the methods of synthesis of chemical compounds but the possible ways in which the specified chemical system can react taking into account the reaction mechanisms and the laws of physical organic chemistry. The "ASSOR" program has many features in common with the "EROS" system (they sprang from a common root—the "MATCHEM"—"CICLOPS" systems), but "ASSOR" is distinguished by a more detailed stage-by-stage examination of the transformations generated in the specified chemical system. The machine search in the "ASSOR" systems can be prosecuted in both the synthetic and retrosynthetic directions, in contrast to the "AHMOS" and "CAMEO" programs. For the description of the "FLAMINGOES" and "EPOS" programs, see Sections VIII and VI respectively.

IV. REPRESENTATION AND ANALYSIS OF CHEMICAL STRUCTURES

As already stated, the functioning of any CS program begins with the input of certain initial data based on information about the structure of the specified chemical system. Virtually all CS programs have at the present time the facility for the input of the structure of a specified CS in the form of a figure with the aid of special graphical devices (graphical display, light pen, etc.).[68] The figure is input as a rule in the form to which the user is most accustomed. The graphical information obtained is transformed into an internal representation of this structure in the program. We shall consider the main principles of the coding of the molecular structure in computer programs, because even at this stage it is possible to determine which particular aspects of molecular structures are the most important for the solution of CS problems.

Any CS program takes into account in the first place the types of atoms in the specified chemical system and the bonds between them, including the multiplicity of the bonds. In other words, a common feature of all the programs is the representation of the structure by a chemical multigraph and its Adjoint matrix.[69] In a number of CS programs, the so called "connection tables", based on the Adjoint matrix of the corresponding multigraph, are used[1,70] for the description of the structure of a chemical compound. The connection tables can also contain additional information about the specified chemical system, for example, they can describe the stereochemical characteristics of the structure[11,24,40,71-75] and atomic charges.[18,39,40,53] In the "SYNGEN" program, the description of the specified chemical system includes only the atoms of the skeleton and the bond between them. Furthermore, for each atom of the skeleton provision is made in the connection table for a "functionality" column, indicating the character of the bonds between the given atom and particular functional groups (FG).[61,76]

The "EROS" program retains the description of the structure in the form of a *BE* matrix, which indicates the bond orders between the atoms of the specified chemical system (non-diagonal elements) and the number of free electrons in the outer valence shell of each atom (the matrix diagonal).[29]

The "SYNCHEM" program[55] uses both the usual representation of structures in the form of connection tables and in the form of the Wiswesser line-formula notation (WLN). The description of the specified chemical system in the form of a connection table is used in the analysis and transformations of structures, while the Wiswesser notation is convenient for the storage and compilation of structural data banks and libraries. Furthermore, the programs are associated with the library of available substances, compiled on the basis of the catalogue of the Aldrich Company in which the reagents are described precisely with the aid of the Wiswesser notation.

In the course of the analysis of the structures forming part of the composition of the specified chemical system, the CS programs extract additional information necessary for further work, namely the characteristic features of the structure of the skeleton (the number and interlinking of the rings and chains), the number and form of the FG, the symmetry of the structure, stereochemistry, etc. The structure is analysed as a rule under automatic conditions in a special recognition unit.[77-87]

V. EMPIRICAL AND NON-EMPIRICAL COMPUTER-ASSISTED SYNTHESIS

Before proceeding with the description of various ways of representing chemical reactions in CS programs, one should note that there are various types of access to these formalised descriptions. At this stage it is in fact possible to differentiate two fundamentally different approaches: the empirical CS, where the transformations of a specified chemical system are effected on the basis of coded information about known organic reactions, and the non-empirical CS, where the transformations are generated by logical-combinatorial procedures without resorting to factual information. In the former case, chemical reactions must be compiled beforehand in the form of a library, while in the latter a set of logical instructions and/or a combinatorial algorithm, which directly generates the transformations, is used to search for the transformations in the specified chemical system.

The advantage of the empirical approach is that the program predicts as a rule entirely probable methods of synthesis and the majority of the selection criteria are contained implicitly in the description of each specific reaction. On the other hand, such programs are linked to a specific library of reactions and are incapable of suggesting a fundamentally new synthetic pathway or finding a new reaction. The non-empirical CS programs are free from this disadvantage, but they require the inclusion in the program of rigorous selection criteria in order to avoid the generation of unrealistic or chemically uninteresting results. At the present time many non-empirical CS programs include also the interaction with data banks by resorting to which it is possible to assess chemically the results obtained, i.e. it is possible to realise an empirical selection criterion.[13,18,61]

VI. REPRESENTATION AND ANALYSIS OF CHEMICAL REACTIONS

The main stage in the computer-assisted planning of synthesis is the search for reactions effecting transformations in specified chemical systems. It is significant that, for the solution of the problem of retrosynthesis, it is essential to consider retroreactions ("antithetical reactions" or "transformations"[1]), i.e. reactions which are the opposite of those which result in the formation of a specified chemical system. Different terminology is used in the literature for the designation of such reactions. Strictly speaking, the term "redistribution of bonds" reflects most accurately the formalised character of the representation of chemical reactions in CS programs, but in the present review we shall employ the term "transformation" as the most widely used.

The majority of CS programs refer to the empirical approach and use in their execution libraries of transformations (LT).[1,11,40,44,50,51,53,57,64,66] It is possible to differentiate the following common features of all LT. Firstly, the description of the transformation includes the enumeration of the structural fragments which must be present in the specified chemical system in order that the given transformation can be effected. Secondly, the description contains a set of different tests, which determine the possibility, in principle, of effecting the given transformation in the specific chemical system and/or determine the priority ("rating") of the transformation described. Furthermore, the description also includes a list of the structural changes which must be carried out in order to generate the structures corresponding to the result of the application of the given transformation to the specified chemical system. Finally, an identifier must be present for each transformation.

The aspects listed above are characteristic of all LT described in the literature,[11,40,55,88] but, depending on the specific features of the concrete CS program, the description of the transformations can be supplemented by additional information. For example, in the "LHASA" and "SECS" programs, a "character" is attributed to each transformation, i.e. an abbreviated specification of the structural changes in the specified chemical system induced by the given transformation (the formation or dissociation of a bond, ring opening or closure, the introduction, removal or modification of FG, etc.).[11,40] Furthermore, the LT of the "LHASA" and "SECS" programs contain information about the reaction conditions (temperature and auxiliary reagents) and also literature references. In the "REACT" system (Govind and Powers),[51] much attention has also been devoted to the description of the technological conditions for the successful occurrence of specific processes.

The description of transformations in Bersohn's program includes the indication of the yield of the corresponding synthetic reaction and additional tests analysing the correctness of the structures obtained as a result of the given transformation.[88]

The "LHASA"[39–41] and "SECS"[11] programs have the largest and most highly organised LT. The transformations are recorded in these libraries in special languages (CHMTRN in the "LHASA" program and ALCHEM in the "SECS" program), which combine the rigorous logical constructions of the algorithmic machine language and an English vocabulary comprehensible to the chemist.

Gelernter uses a different form of description of transformations, which is closer to the machine interpretation.[55] The set of tests which must be performed on the structure of the specified chemical system is represented by Boolean functions.[89] As a result of the successive operation of these functions, special codes are produced, which enables the program to reach a conclusion about the applicability of the transformation, to attribute to it the appropriate rating, or to report that another transformation must be resorted to in a preliminary step.

the "EPOS" system, the first empirical CS program in the USSR, is being developed at the Scientific-Information Centre for Molecular Spectroscopy of the Novosibirsk Institute of Organic Chemistry of the Siberian Division of the USSR Academy of Sciences.[67] The program is designed for retrosynthetic planning of organic synthesis using a library of transformations; in terms of the form of access to the LT, the system is similar to Gelernter's program.

In contrast to the empirical CS programs, in the programs based on the non-empirical approach, the transformations of a specified chemical system are effected as a result of the application of certain logical instructions and not on the basis of a bond redistribution scheme obtained from the LT.[13,16,18,27,28–34,42,61,62]

The "EROS" and "TOSCA" programs employ sets of "reaction generators", i.e. instructions which describe in the most general form the bond redistribution in the course of chemical reactions.[29,30,62] In the latest version of the "EROS" program,[30] five reaction generators are used, which when combined describe the majority of organic reactions: (1) X: + I–J → I–X–J; (2) I–X–J → X: + I–J; (3) I–J + K–L → I–K + J–L; (4) I–J + K–L + M–N → N–I + J–K + L–M; (5) I–J + K–L + X: → J: + I–K + L–X, where I, J, K, L, M, and N are reaction centres, i.e. atoms linked by bonds which undergo a change in their order by unity. The dissociation of the "bond" between the centres I and J in the reaction generator can imply both real dissociation and a decrease of the bond order in the specified chemical system: analogously the formation of a "bond" in the reaction generator can correspond both to the real formation of a bond and to an increase of the multiplicity of the bond already present. The centre X: corresponds to an atom whose valence changes by two units in the course of the reaction, for example, the carbene centre in the carbene addition reaction. The functioning of the "TOSCA" program is based on reaction generators analogous to the generators (3) and (4). An additional transformation of the type I–J–K + L–M → I–K + L–J–M is also used.[62]

Evidently the same reaction generator can give rise to different chemical reactions for different centres and bonds in the chemical system. For example, the generator (3) can correspond both to addition to the double bond and to a substitution reaction. Thus reaction generators applied to a specific chemical system can give rise, together with well known reactions, to completely new transformations.

The description of the reaction mechanism constitutes a specific feature of the "ASSOR" program,[16,17] which operates with only four transformations (principal reactions). These transformations correspond to oxidation–reduction processes ($I^{\cdot} + J \rightleftarrows I + J^{\cdot}$ and $I^{-} + J^{+} \rightleftarrows I^{+} + J^{-}$) and to dissociation–association processes ($I{-}J \rightleftarrows + I^{+} + J^{-}$ and $I{-}J \rightleftarrows I^{-} + J^{+}$), which are represented in the most general form. Such representation of the transformations is in many respects analogous to the reaction generator in the "EROS" program, aut the "ASSOR" system pays more attention to the reaction mechanism, which entails an increase of the number of CS stages. For example, four search stages in the "ASSOR" program correspond to the result of the operation of the generator (3) (one stage of the machine search in the "EROS" program).

The "AHMOS" system[12,13] uses a formalised representation of organic reactions, which is also in many respects analogous to the representation of reactions in the "EROS" program. The principal differences consist in the fact that, firstly, the transformations in the "AHMOS" program are more specific than the reaction generator, because they contain an indication of the type of reaction centre (electrophile, nucleophile, etc). Secondly, the transformations in the "AHMOS" program correspond in fact to the elementary stages of organic reactions and not to the overall result of the process. Weise[13] considers the transformations corresponding to the following processes:

(1) addition: $E + Nu \rightarrow E^{-}{-}Nu^{+}$;

(2) substitution: $EFABG{-}NFABG + Nu \rightarrow EFABG{-}Nu^{+} + {}^{-}NFABG$;

(3) dissociation: $EFABG{-}NFABG \rightarrow {}^{+}EFABG + {}^{-}NFABG$;

(4) protonation: $X{-}H + Nu \rightarrow X^{-} + Nu^{+}{-}H$;

(5) sextet rearrangement; $Y{-}X{-}Z \rightarrow X^{+}{-}Z^{-}{-}Y$;

(6) polarisation: $X^{-}{-}Z \rightarrow X{=}Z^{-}$ or $X^{-}{-}Z{=}Y^{+} \rightarrow X{=}Z{-}Y$;

(7) electrophilic substitution: $E + H{-}C(Ar) \rightarrow E^{-}{-}C(Ar) + H^{+}$;

(8) elimination: $Nu + H{-}X{-}EFABG{-}NFABG \rightarrow X{=}EFABG + H{-}Nu^{+} + {}^{-}NFABG$.

Here E is an electrophile, Nu a nucleophile, EFABG and NFABG are respectively electrofugitive and nucleofugitive leaving groups, and X, Y, and Z are other reaction centres (Z is a sextet atom).

The non-empirical CS program "FLAMINGOES"[31-34] can operate with both multistage chemical reactions (with an arbitrary degree of complexity) and with individual stages of the mechanism. The universality of the "FLAMINGOES" computer system compared with other non-empirical CS programs is achieved by using not an individual extremely limited set of reaction generators but a general combinatorial algorithm in the course of the execution of which the most varied chemical reactions and/or reaction stages can be generated, including completely new or little investigated processes (for a more detailed description of the "FLAMINGOES" system, see Section VIII).

The program "SYNGEN"[60,61] is based on a novel classification of organic compounds by Hendrickson.[90-95] This system is also based on the claim that the majority of organic reactions can be represented as a change in the immediate environment at one or several carbon atoms on passing from the initial compounds to the products (or in retrosynthesis on passing from the specified chemical system to the precursors). It is suggested that the entire wide variety of the possible environments of a carbon atom can be expressed by four bond types:

(1) type H: σ-bond with a hydrogen atom or an atom less electronegative than hydrogen;

(2) type R: σ-bond with another carbon atom;

(3) type Π: π-bond with another carbon atom;

(4) type Z: σ- or π-bond with an atom more electronegative than hydrogen.

The number of bonds of each type is designated respectively by h, σ, π, and z; evidently, $h + \sigma + \pi + z = 4$. Hendrickson calls the sum $f = \pi + z$ the functionality of the carbon atom. In this system any reaction will be defined if the change in the environment at all the carbon atoms on passing from one chemical system to another is specified. For an individual carbon atom, this change is designated by two letters: the first characterises the type of bond formed and the second the type of bond ruptured. Thus altogether there is a possibility of $4 \times 4 = 16$ types of structural changes at the carbon atom.

Hendrickson divided the entire set of organic reactions into three classes. The first class includes constructive reactions, i.e. reactions as a result of which the carbon skeleton of the organic compound is altered. Constructive reactions involve three types of structural changes: RH, RΠ, RZ. The trans-functionalisation reactions (the introduction, elimination, or alteration of the FG), including nine types of structural changes, namely HH, HZ, ZH, ZZ, ΠH, ΠZ, HΠ, ZΠ, and ΠΠ, belong to the second class. The remaining four types of changes in the environment of the carbon atoms refer to destructive reactions, which are not used in the "SYNGEN" program.

Among all the constructive reactions, the "SYNGEN" program employs only those in the course of which a single C–C σ-bond is formed and the environment changes at not more than three carbon atoms in the chain on either side of the bond formed. For such constructive reactions and also for the trans-functionalisation reactions, lists of instructions are stored in the program in a coded form and ensure the execution of the necessary transformations in the specified chemical systems; these instructions are also referred to as half-reactions. On the one hand, the compilation of such instructions does not involve the use of factual data from organic chemistry, but, on the other, the set of possible half-reactions is stored in the computer memory like the libraries of transformations in the empirical CS programs. Consequently Hendrickson's method is to some extent intermediate between the empirical and non-empirical CS.

VII. THE SELECTION CRITERIA

In the previous Sections it was shown how the chemical information in the known computer systems is formalised and coded. However, as already stated, the most important problem in CS is the creation and formalisation of selection criteria whose operation in fact imparts to the CS programs the features of an "artificial intelligence".

In empirical CS programs, the selection criteria can be used in three main stages of the search: (1) the choice of a definite "strategy of the synthesis", which limits the number and form of the transformations available in the LT; (2) the assessment or grading of concrete transformations before their use in the specified chemical system; (3) the assessment or grading of concrete precursors of the given chemical system obtained as a result of the transformation.

"The strategies of the synthesis", which make it possible to direct the machine search in a specified direction, have been developed to the greatest extent in the "LHASA" and "SECS" programs. We shall list the main types of such strategies.[11,35,39-41]

1. "The strategy of applicability", i.e. the search in the LT for all the transformations which are applicable to a specified chemical system. The main disadvantage of this strategy consists in the fact that large classes of transformations, such as the introduction, removal, or modification of FG are almost always applicable, which leads to an appreciable growth of the "synthesis tree".[11,35]

2. Strategies designed to achieve the transformations, i.e. the search in the LT for known sufficiently reliable reactions with the aid of which it is possible to carry out an elegant synthesis of specified chemical systems.[41] Such reactions include, for example, the following processes: the Diels–Alder reaction, the Robinson annelation, the Aldol condensation, and sigmatropic rearrangements. Another variety of strategies designed for transformations consists in the construction with the aid of the simplest, "mechanistic" transformations (the addition of a proton, the removal of a proton, etc.) of the possible mechanisms of the formation of the specified chemical system.[41]

3. Structurally oriented strategies, i.e. the search for transformations leading precisely to precursors of the specified chemical system which contain definite structural fragments.[11,41]

4. Topological strategies, i.e. the search for transformations leading to the rupture of one or several "strategic" bonds as a result of which the structure of the initial chemical system may be appreciably simplified.[11,41,96]

5. Stereochemical strategies, i.e. the search for transformations with the aid of which it is possible to synthesise the specified chemical system with a definite configuration of all the stereocentres.[41]

6. Strategies oriented towards functional groups, i.e. the search for transformations which effect the introduction, removal, protection, or modification of FG. This strategy usually precedes the application of other strategies, whose direct application is frequently difficult precisely because of the presence in the specified chemical system of concrete functional groups.[11,41,97–99]

The selection of a definite strategy can be achieved automatically or with participation of the user. The application of several strategies makes it possible as a rule to find extremely effective and elegant methods of synthesis.[40,41]

In the programs of Bersohn[63,64] and Gelernter[55–57] access to the LT is achieved on the basis of data obtained in the course of the analysis of the structure of the specified chemical system or, in other words, "the strategy of applicability" is carried out. In Bersohn's program, the application of this strategy is rigorously ordered. Firstly, all the structural fragments found by the computer in the recognition unit receive different ratings. The highest rating is given to structural fragments in the formation of which the greatest number of bonds are formed simultaneously, as happens, for example, in the formation of a three-membered ring in the Simmons–Smith reaction and of a six-membered ring in the Diels–Alder reaction.

Secondly, the reactions in each section of the LT are also arranged in order of decreasing priority of the corresponding synthetic reactions. The highest rating is given to the reactions involving the introduction of FG; next follow the reactions leading to the construction of the molecular skeleton, the isomerisation reactions, and the reactions leading to the protection of the FG, the removal of the protection, the modification of the FG, and the elimination of the FG. Fragmentation reactions have the lowest rating, because the corresponding transformations complicate the structure of the specified chemical system.[64]

One of the most fundamental and hitherto unsolved problems of organic chemistry—the problem of the *a priori* estimation of the probability of the occurrence of the reaction—is solved in CS programs with the aid of formal and empirical selection criteria. The transformation is regarded as formally feasible if the given chemical system contains a structural fragment formally essential for the execution of the given transformation. Empirical selection criteria are based on a more profound analysis of the structure of the specified chemical system, the reaction conditions, the reactants, etc. The final assessment (rating) of the transformation is determined as a result of a series of tests, which are as a rule contained in the description of the transformation itself.[11,39,40,55,88] The information obtained in the recognition unit is most actively employed precisely at this stage. For a more detailed analysis of the transformations, additional information may be resorted to.

Additional selection criteria have been developed most in the "SECS" program.[11] Thus the applicability of a particular transformation from the LT is determined not only by the results of the tests contained in the description of the transformation but also in conformity with a specified "list of aims", which contains information about the required changes in the skeleton on the FG. In conformity with this list, the transformations of the LT are rejected if the character of the transformation does not correspond to any of the "aims" in the list. If the transformation satisfies the given criterion but the structural fragment indicated in the description of the transformation differs from the structural fragment of the specified chemical system only by the presence and/or type of FG, then, before the direct application of the transformation, the "SECS" program carries out the necessary modification of the structure (in the "LHASA" program the strategy oriented towards the FG operates analogously).

In the first version of the program "SECS" much attention was already devoted to allowance for the steric and electronic effects in assessing a specific transformation. The subprogram "SYMIN" constructs in the computer memory a three-dimensional model of the specified chemical system using calculations by the method of molecular mechanics. In order to estimate the probabilities of reactions with participation of coupled systems, the calculations of molecular orbitals by the Hückel method are used. Depending on the results obtained, the rating of the transformations selected from the LT may be altered.

An important criterion of the applicability of selected transformations is a test designed to show that the conditions favourable for the occurrence of the corresponding synthetic reaction would induce undesirable changes in the specified chemical system. The "SECS" program analyses the sensitivity of various FG under the conditions of the given reaction and selects the protecting reagent. If the reaction conditions and the structure of the specified chemical system preclude a satisfactory protection of the FG, the transformation is regarded as unsuitable.

In the absence of information about the symmetry of the specified chemical system, the application of the same transformation to a structure having several symmetry elements inevitably leads to the duplication of results. The "SECS" program determines the entire symmetry group of the three-dimensional model of the specified chemical system, which makes it possible to generate subsequently only non-equivalent results.

Bersohn's[63,64] and Gelernter's[55–57] programs operate non-interactively, generating the methods of synthesis of the specified chemical system without interference by the user. Consequently the selection criteria underlying these programs must be more rigorously formalised than the criteria in the "LHASA" and "SECS" programs. Thus in Bersohn's program the transformations within a single class of priority are assessed by a special rating which is higher the higher the yield of the corresponding synthetic reaction.[88]

In an earlier study, Bersohn and co-workers[63] used additional criteria for the assessment of individual stages of the synthesis. Each transformation received its rating, which was characterised in terms of arbitrary units by the "simplification"/"cost" ratio. The value of "simplification" increased if the transformation resulted in a decrease of the number of rings, the number of FG, and the number of non-hydrogen atoms. The "cost" depended on many factors, including the yield of the reaction.

In the "SYNCHEM" program[55–57] each transformation is assessed rigorously in conformity with a set of tests in the form of Boolean functions. These tests embody many of the heuristic rules by which the chemist is guided in assessing a chemical reaction. On the basis of the results of these tests, the initial rating of the transformation can be altered (for example, it can be increased if a conjugated activating group is present or it can be reduced if the transformation is interfered with by steric hindrance). The successive application of the Boolean functions can result in a partial modification of the very scheme of the transformation. For example, if a FG sensitive to the reagent used during the reaction is found, then the program can introduce another reagent or can resort to a procedure involving the protection of the FG.

Together with the assessment of the transformations, the precursors themselves are assessed in empirical CS programs. For example, in the "SECS" program[11] different variants are rejected with the aid of the following structural selection criteria: the breakdown of Bredt's rule; the presence of an antiaromatic system; the presence of a cumulated system; a triple bond in a small ring; a *trans*-olefin in a small ring; a cyclic system with a bridge in the *trans*-position; *trans*-condensed three-membered rings; an incorrect valence of an atom; two charges of identical sign on different atoms; an unstable combination of FG. Analogous selection criteria for structures are applied in the majority of both empirical and non-empirical CS programs.

Apart from the criteria testing the formal correctness and "chemical significance" of the structure generated, a very effective criterion, determining the completion of the construction of the synthetic chain in the specified chemical system, is used in a number of non-interactive CS programs designed for retrosynthesis.[55,56,60,61,63,64] In order to apply this criterion, the program must be supplemented by a special data bank—the library (catalogue) of the available substances (DBS). If the structure of the successive precursor generated in the course of the machine search is identical with one of the structures stored in the DBS, the construction of one of the possible synthetic pathways is regarded as completed. Bearing in mind that the reactions leading to the introduction, removal, or modification of FG play a secondary role compared with the reactions involving the construction or modification of the skeleton, one may assume that agreement to within the number and form of the FG is sufficient to satisfy the given criterion.[60,61]

The main problem encountered by non-empirical CS programs is that of the selection from the entire set of the possible synthetic pathways of the most probable and interesting from the chemical point of view. In the non-empirical programs, it is possible to differentiate subproblems in the solution of which selection criteria are employed: the limitation of the types of transformations generated in a concrete specified chemical system; the limitation of the applicability of the transformations in the specified chemical systems; the evaluation or rejection of the generated precursors of the specified chemical system. The selection criteria for the precursors[18,62] are in many respects similar to the analogous criteria in empirical CS programs, and we shall therefore transfer the centre of attention of our discussion to the specific features of the selection criteria of the first two types in non-empirical CS programs.

The possibility of selecting the types of transformations which can be generated in the specified chemical system in an explicit form is present in the "EROS" program,[29,30] where, firstly, provision is made for the situation where the user excludes from the list of reaction generators stored in the computer memory those which correspond to the processes which in his view cannot lead to the specified chemical system. With the user's implicit agreement, it is assumed that all five reaction generators can be applied to the search for the precursors of the specified chemical system. Secondly, there is a possibility of imposing definite limitations on the form and size of the "synthesis tree".[30] In particular, one can seek the maximum number of levels of the "synthesis tree" (the number of CS stages), the number of precursors at each stage, the maximum number of precursors generated for a single chemical system, and the maximum number of precursors which can be regarded as specified by the chemical system in the next CS stage.

The main principle in accordance with which the types of transformations are selected in the "SYNGEN" program[60,61] is that the planning of the synthesis must be based in the first place on the constructive reactions, i.e. reactions in the course of which the skeleton of the specified CS is formed. The trans-functionalisation reactions in the course of which the FG are modified but the molecular skeleton is unaffected are regarded as auxiliary.

As shown in Section VI, the description of any transformation in the non-empirical CS programs in a general form can be represented as a set of reaction centres with an indication how the bonds between them are distributed. Consequently the selection criterion which can limit the applicability of particular transformations consists in the selection of the potential reaction centres or reactive bonds from the entire set of atoms and bonds in the specified chemical system.

In the "EROS" program,[29,30] the given criterion is applied in the analysis of the structure of the specified chemical system in the course of which the bonds capable, in principle, of rupturing during subsequent transformations are determined. Such bonds can be recognised both automatically and with participation of the user. In the automatic mode, the multiple bonds, the C–X, H–X, and X–X bonds (X is a heteroatom), as well as the adjoining bonds are revealed as reactive. Aromatic bonds are not regarded as reactive. The user can arbitrarily correct the list of reactive bonds initially formulated by the computer. Furthermore, the user can specify the optimum enthalpy of the reaction and the range of the permissible enthalpies. For each transformation generated by the computer, the enthalpy is calculated in accordance with Allen's scheme.[100–103] Gasteiger[103] claims that this in general non-rigorous approach yields a satisfactory agreement with experimental data and can serve for a rough estimation of the probability of the reaction. If the calculated reaction enthalpy falls within the range of permissible values, the transformation is regarded as probable; otherwise the precursor found by the computer is rejected. The specified optimum enthalpy makes it possible to estimate in detail the probability of the process predicted by the computer. The closer the calculated reaction enthalpy to the specified value, the higher the rating of the transformation and the corresponding precursors will be investigated in the first place in the next CS stage. We may note that the "CHIRP" program, which is related to the "EROS" system, uses the calculated Gibbs free energies for the estimation of the probability of the transformations in the specified chemical system.[27]

Gasteiger and co-workers have also carried out studies designed to create non-empirical selection criteria for reactive bonds, criteria based on a quantitative determination of the partial atomic charges,[104,105] inductive[106] and resonance[107] effects, dipole moments,[107] and polarisability effects.[108] Iterative procedures, which make it possible to determine the distribution of partial charges in simple compounds with small numbers of atoms, containing heteroatoms, have been described.[104,105] On the basis of the data obtained, it is possible to calculate the C–X (X is a heteroatom) bond energies,[105] the pK_a,[105] and $J(^{13}C{-}H)$,[109] and the proton affinities.[106,108,110,111] It may be hoped that in its subsequent development the method based on the partial balancing of the orbital electronegativity[105,112] will indeed make a significant contribution to the creation of a general theory of the reactivity of organic compounds, but at the present time the selection of reactive bonds on the basis of topological and structural characteristics constitutes a more general, faster, and more reliable method.

The "TOSCA" program[62] employs an interesting and novel method for the limitation of the applicability of transformations in the specified chemical system. Like the empirical CS programs, the operation of the "TOSCA" system is based on the selected strategy of the synthesis. The program employs two strategies: consonant and dissonant. The consonant strategy consists in the search for nucleophilic and electrophilic substitution and addition reactions. The dissonant strategy involves the search for oxidation and reduction processes—reactions leading to a change in polarity. In contrast to the empirical programs, in the "TOSCA" program the strategy is chosen precisely as the stage corresponding to the selection of the potential reaction centres and reactive bonds. All the atoms incorporated in the specified chemical system, starting with the heteroatoms, are designated by the "+" or "-" sign in accordance with their electrophilic or nucleophilic properties. If all the bonds are consonant in the specified chemical system, i.e. there is not one pair of adjacent atoms with identical charges, preference is given to the consonant strategy.

For a specified chemical system containing dissonant bonds (adjacent atoms with identical signs), it is possible to select both a dissonant and a consonant strategy. In the consonant strategy, limitations are imposed on the operation of transformations: bonds may be formed only between atoms with opposite signs while dissonant bonds are revealed as unreactive. On the other hand, the dissonant strategy permits the recombination of atoms with identical signs.

The logic of the "SYNGEN" program[60,61] is based on the idea of "ideal synthesis" as a sequence of constructive reactions.[10] For this reason, bonds in the molecular skeletons incorporated in specified chemical systems are chosen exclusively as the reactive bonds. The "SYNGEN" program initially seeks all possible ways of subdividing the skeleton into constituent components—synthons. In the general case, the number of subdivisions can be very great and additional criteria for the evaluation of the effectiveness of a particular set of synthons for the synthesis of specified chemical systems are therefore necessary. On the basis of the concept of "ideal synthesis", Hendrickson introduces the criterion of convergence.[10,60,95] In convergence synthesis, the fragments of the target structure are formed independently and are combined only at the end of the synthesis. In conformity with this requirement, the subdivision of the skeleton of a specified chemical system in the first stage should lead to two synthons with approximately equal numbers of atoms, to four such synthons in the second stage, to eight synthons in the third stage, etc.

In the course of a single subdivision of the skeleton, the rupture of one to two bonds and the closure of at most one ring are permitted. Preference is given to subdivisions for which the "reassembly" of the molecule is described by effective synthetic reactions, for example the Diels–Alder reaction. It is essential to differentiate the situation where the synthons obtained as a result of the subdivision of the skeleton are found to be identical, since the synthetic scheme simplifies greatly in this instance. Apart from the identity or similarity of the synthons, a test is made to discover if each synthon found is present in the DBS. For synthons which are absent from the DBS, the subdivision operation is repeated.[60,61]

Each sequence of subdivisions of the skeleton of the specified chemical system, leading to synthons for which correspondences in the DBS have been found, generates the so called "ordered bond set".[60] This set consists of bonds which must be broken in a specific sequence in order to obtain the specified subdivision into synthons. The bonds entering into the given set are considered in succession in the same order and all the suitable (on the basis of the presence of concrete FG in the specified chemical system) constructive half-reactions or, where necessary, transfunctionalisation reactions are applied to each bond. This results in the discovery of not only the skeletons of the initial compounds but also of the FG present in these compounds.

As already stated, the "AHMOS"[12-15] and "CAMEO" systems occupy a special place among the CS programs. In terms of the character of the representation of the structure of the transformations, these programs are close to the "EROS" and "LHASA" systems respectively. The "AHMOS" program has come to be classified as a non-empirical CS, while the "CAMEO" system, based on several small data banks, occupies an intermediate position between the non-empirical and empirical systems. We placed the special discussion of the "AHMOS" and "CAMEO" programs in the Section devoted to the selection criteria, because novel criteria based on the laws of physical organic chemistry in fact constitute an inseparable feature of these programs.

Pearson's classification of acids and bases serves as the basis of the selection criteria used by the "AHMOS" program.[12,13] Weise considers six types of reaction centres: a hard electrophile, a soft electrophile, a hard nucleophile, a soft nucleophile, a nucleofuge, and an electrofuge. The program has a small data bank in which the reactivity indices of different FG, reflecting quantitatively the nucleophilic and electrophilic properties of these groups, are stored. On the basis of the scale of evaluations introduced, all the FG found by the program in the recognition unit receive their rating—the reactivity index. Subsequently the program uses these ratings to calculate another quantitative characteristic—the "tendency to react" index for different modes of interaction of electrophiles and nucleophiles provided for by the program (see Section IV). The values obtained are compared with the specified threshold values and the transformations whose occurrence is most preferred in the specified chemical system are thus determined. The program effects priority transformations, generating thereby the possible products of the reaction of the specified chemical system.

The criteria for the evaluation and selection of the possible mechanisms of an organic reaction have been specially developed in the studies of Jorgensen and co-workers.[18-26] The "CAMEO" program for the prediction of the reaction products when the starting materials and the reaction conditions are specified has been created on the basis of these criteria. It is noteworthy that the program carries out the search in the forward (synthetic) direction and is designed not so much for the generation of whole reaction sequences as for the evaluation of the possibility of the occurrence of a particular reaction in different directions. The program has several units, each of which is designed to work with a definite class of reactions. Overall, the "CAMEO" program covers the following processes: interaction of electrophiles and nucleophiles under the conditions of base catalysis[18] including certain reactions of organometallic compounds,[19] the reactions of organosilicon compounds,[19] pericyclic reactions,[21,22] and nucleophilic and electrophilic substitution in aromatic compounds.[23-25] For each of these classes of reactions, special criteria estimating the probability of the process in a particular direction have been developed.

We shall consider in greater detail the criteria for the selection of transformations interpreted in the "CAMEO" program as the reactions of electrophiles and nucleophiles under the conditions of base catalysis.[18] The potential reaction centres are selected as follows: with the aid of a small data bank and a special algorithm,[26] the program determines the most acid protons and generates transformations corresponding to the transfer of protons to the base. The atoms to which the protons are linked are regarded as potential reaction centres—nucleophiles. For organometallic compounds,[19] account is also taken of the possibility of the occurrence of competing addition and exchange reactions. The processes leading to a weaker base are regarded as dominant.

The potential electrophilic centres are determined from structural characteristics (for example, a multiple bond) and also from the pK_a of the leaving group taking into account the specified reaction conditions. With the aid of a set of heuristic rules and data on the structure of the reactants and the character of the FG obtained in the recognition unit, the possibility of the occurrence of competing addition, substitution, and elimination processes with participation of nucleophilic and electrophilic reaction centres is determined.

Subsequently this unit of the "CAMEO" program underwent significant modifications and includes at the present time also the recognition and investigation of reactions with participation of organosilicon reactants[20] and vinyl and aromatic electrophiles.[23]

The functioning of the unit for the study of electrophilic substitution reactions in aromatic systems[25] is based on the determination of the potential reaction centres participating in the process. The most important procedure in this unit is the calculation of the relative reactivities of different centres in the aromatic system. Depending on the reaction conditions and the type of aromatic system (substituted benzene, a heterocycle, a polycyclic system), an initial relative reactivity index is assigned to the system. Using the data obtained in the analysis of a specified chemical system in the recognition unit and the set of heuristic rules, the program takes into account the influence of substituents. An equation has been derived for the calculation of the correction to the initial index as a function of the number and type of electron-donating and electron-accepting substituents. After the calculation of the relative reactivity indices of the aromatic systems as a whole, the program proceeds to determination of the different reaction centres in each system, being guided by the set of heuristic rules. Account is taken also of the steric effect of the substituent.

The stereochemical selection criteria play a major role in the study of pericyclic reactions.[21] Thus dienes are assumed to be unreactive if steric hindrance prevents them from attaining the *S-cis*-configuration. Apart from the stereochemical criteria, various heuristic rules can be used for the selection of reactive dienes, dienophiles, 1,3-dipoles, and dipolarophiles. The main criterion for the selection of pericyclic reactions is applied in the comparison of the energies of frontier orbitals. It is assumed that the lower the difference between these energies, the easier the cycloaddition. Furthermore, the program predicts the relative regioselectivity and stereoselectivity of the process from the results of the calculation of the energies of the frontier orbitals. The energies are determined from the ionisation potentials taken from the special data bank of the "CAMEO" program.

The analysis of [2 + 2]cycloaddition reactions, [2,3]- and [3,3]-sigmatropic rearrangements, and $[1,j]$ shifts of σ-bonds ($j = 3,5,7$)[22] was subsequently included in the program. In order to estimate the priority of a particular reaction pathway, the activation energies calculated on the basis of the analysis of a large number of experimental kinetic data for reactions of the types enumerated were used. Contrary to the authors' expectation,[21] it was found that the enormous variety of the rates of pericyclic reactions and the influence of too many factors on the rate of reaction are all causes which preclude at the present time the development of general principles for the estimation of the probabilities of pericyclic reactions.

VIII. THE UNIVERSAL COMPUTER SYSTEM "FLAMINGOES" FOR THE SOLUTION OF PROBLEMS OF SYNTHESIS AND FOR THE DETERMINATION OF REACTION MECHANISMS IN ORGANIC CHEMISTRY

The "FLAMINGOES" computer system (Formal-Logical Approach to Molecular Interconversion. Non-Empirical Generation, Orientation, and Evaluation Synthesis) constitutes a novel development in the application of computers to organic chemistry achieved by the authors of this review.[31-34] The formal-logical approach, developed previously by Zefirov and Trach,[113-119] is used for the formal specification of the chemical information used in the given system. The general treatment of the chemical processes, based on this approach, made it possible to create the given universal computer system, which is suitable for the solution of any problems of organic chemistry formalised as a constructive list of bond redistributions in chemical structures. The principal types of problems to the solution of which the "FLAMINGOES" system can be applied are, firstly, computer-assisted synthesis, secondly, the study of rearrangements, and, thirdly, the prediction of the mechanisms of complex multistage reactions.

We shall consider briefly the representation and analysis of chemical reactions in the "FLAMINGOES" system. The most important types of organic reactions are formally described as a result of a cyclic bond redistribution (CBR) in the initial chemical system, which leads to the formation of the final chemical system.[113] Consequently, an alternative approach to the solution of the CS problem (alternative to the use of a LT or a set of reaction generators) is a systematic unrepeated generation of all possible CBR in the specified chemical system, which permits the finding of a complete set of the possible precursors of the specified structure (in retrosynthesis) or the complete set of products of the possible reactions in the initial chemical system (in forward CS). If the results obtained are promising for further study, the procedure involving the generation of transformations (in the form of CBR) can be extended to several stages.

The "FLAMINGOES" system, which is based on a systematic unrepeated generation of CBR, has no direct analogies among foreign programs. Retaining all the advantages of the non-empirical approach (the generation of transformations independently of data banks, the possibility of operating with new or little investigated reactions), the "FLAMINGOES" system approaches empirical programs as regards the breadth of coverage of chemical data, since ~90% of the known chemical reactions can be described as processes with CBR and hence such processes can be generated by the "FLAMINGOES" system in the course of the solution of problems of computer-assisted synthesis.

We shall consider the principal types of selection criteria used in the "FLAMINGOES" system. Firstly, the formal criterion designed to test that the correct valences of the atoms and bond orders are used is introduced.

Secondly, the program uses the following empirical criterion: in order to limit the number of formally correct but chemically uninteresting solutions, the "FLAMINGOES" system can be designed to generate not all the CBR possible in the specified chemical system but only those which correspond to the specified limitations to the size of the CBR and also the limitations to the number of bonds formed and the number of bonds ruptured. The "FLAMINGOES" system is interactive and the chemist can introduce all the limitations into the program in the dialogue mode. It is noteworthy that the permissible dimensions of the CBR and also the numbers of formed and ruptured bonds define the set of permissible transformations in the specified chemical system.[113]

Thirdly, the "FLAMINGOES" computer system uses the equivalence criterion. The generation of the CBR in the chemical system for which the corresponding graph has several automorphisms inevitably leads to repeated results. The operation of the equivalence criterion has been organised in the "FLAMINGOES" system in such a way that one can avoid the duplication of the results already in the CBR generation stage; in order to apply this selection criterion, use is made of the information about the group of automorphisms of the graph corresponding to the initial chemical system. It must be emphasised that all the most important selection criteria in the "FLAMINGOES" program operate at the earliest possible generation stages long before the explicit construction of the final chemical system.

The "FLAMINGOES" program is written in the BASIC language and is designed for the USSR produced personal computer "Iskra 226" (64 K). The present version of the "FLAMINGOES" system includes the main program and nine principal subprograms and occupies 60 kbyte of the computer memory. The average generation time is 3–5 s per result. We shall now consider the principal program units comprising the "FLAMINGOES" system.

1. The input of the initial chemical system. In this unit the chemist introduces the structure of the initial chemical system in the form of a figure on the graphical display. The program uses the Adjoint matrix of the multigraph corresponding to the initial chemical system in order to represent the structure. In this unit the user also specifies the number of stages of the computer-assisted synthesis.

2. Construction of the group of automorphisms. In the course of the execution of the given subprogram, all the automorphic features of the graph corresponding to the initial chemical system are automatically generated. Information about the symmetry of the graph is essential for the generation of only non-equivalent CRB, i.e. for the application of the corresponding selection criterion. The unit designed to construct the group of automorphic features is based on the "AVTOGRAF" [?AUTOGRAPH. Ed. of Translation] FORTRAN package.[120]

3. The input of information necessary for the application of the empirical selection criteria:

(a) The limitation of the applicability of transformations in the specified chemical system (see above): in the present version of the "FLAMINGOES" program, heteroatoms and atoms linked by a multiple bond are automatically revealed as potential reaction centres. The chemist is then able to correct arbitrarily, in the dialogue mode, the set of centres put forward by the computer. In addition, the chemist selects from the set of potential reaction centres those which can undergo a change in their valence. For each selected centre, it is necessary to indicate the permissible variant of the change in valence.

(b) The limitation of the types of transformations generated in the specified chemical system (see above). The chemist is able to introduce the limitations on the permissible size of the CBR and on the number of bonds formed and ruptured.

It is noteworthy that provision is made in the program for the "search without limitations" mode in the course of which all formally possible CBR are generated (with ring sizes from three-membered to eight-membered). This mode makes it possible to discover all the strategic pathways to the synthesis of the specified compound which are possible in principle, especially for structures with few atoms for which the number of solutions will not be unduly great.

4. Unrepeated generation of CBR. This subprogram is the most important combinatorial unit in the "FLAMINGOES" computer system. The rapidity of the operation of this unit determines the rapidity of the operation of the program as a whole. A lexicographic inspection of the "sorting tree", in the course of which all possible CBR are generated taking into account the formal and empirical selection criteria, is effected in module A. Module B applies the equivalence criterion on the basis of information about the group of automorphisms of the graph.

5. The output of the final chemical systems. The structures of the final chemical systems can ae output (if the user so wishes) by the printing device (in the form of digital codes for the corresponding CBR), on the graphical display, and on the printer-plotter (in the form of figures).

6. The selection of results for investigation in the next stage (multi-stage CS). The chemist can select from the set of generated results the final chemical systems which are of interest for further study. The selected chemical systems are stored in a special block within the program itself; when the possibilities for the unrepeated generation of CBR in the specified chemical system have been exhausted, the program selects in succession structures encoded in the above block and introduces them as the initial chemical system in the next stage of the computer search.

The "FLAMINGOES" system has extensive possibilities for the solution of a wide variety of problems in synthetic organic chemistry and for the determination of the mechanisms of organic reactions. The initial chemical system, specified by the chemist in the dialogue mode (see paragraph 1), can contain up to 32 centres, the centres being individual atoms or whole atomic groups, introduced as a single whole. Taking into account the possibilities of the "Iskra-226" personal computer, the number of stages in computer-assisted synthesis which can be stored simultaneously in the operating computer memory does not exceed six, but, when external memory devices are used (for example a magnetic floppy disc), the number of CS stages can be arbitrarily large. The "FLAMINGOES" system makes it possible to operate with any organic structures, including complex polyatomic compounds, heterocyclic and organometallic compounds, and ionic and radical species.

In order to demonstrate the possibilities of the "FLAMINGOES" system, a computer search was carried out and a study was made of the pathways leading to the synthesis of a series of skeletal compounds and rearrangements in families of isomers and of the possible mechanisms of organic reactions with participation of ionic and radical species.[31–34] The investigation demonstrated a satisfactory level of the predictive power of the "FLAMINGOES" system. In the course of the operation of the program, not only were virtually all the literature data on the transformations investigated reproduced but also new novel methods of synthesis, rearrangements, and mechanisms of the reactions of the organic compounds investigated were predicted.[121,122]

IX. PROSPECTS FOR THE DEVELOPMENT OF COMPUTER-ASSISTED SYNTHESIS

At the present time there is no doubt whatsoever that the application of computers is essential for the solution of problems in the planning of synthesis, in the prediction of reaction pathways, and in the study of rearrangements. Furthermore, the formalised representation of chemical information in the computer permits strategic planning of a chemical experiment using new or little investigated processes.

As stated above, computer-assisted synthesis is developing in two directions, namely as empirical and non-empirical CS. At the beginning of their development, the programs for computer-assisted synthesis must fulfill the role not only of the apparatus for the planning of the synthesis, but, to a greater extent, they must serve as an automated reference device for synthetic methods in organic chemistry. Naturally, this role can be managed only by empirical CS systems. However, highly organised data banks for chemical reactions, for example "REACCS",[123] specially designed to be used in the search for known reactions on the basis of specified structural fragments, reaction conditions, etc., appeared in the 1980's. Therefore, the problem of the search for a novel strategy for synthesis, the problem whose exhaustive solution is within the capacity of precisely the non-empirical programs—the "artificial intelligence" systems—has come to the fore at the present time in connection with the solution of problems associated with the planning of syntheses. Therefore, despite the fact that the empirical procedures have been developed to an incomparably greater extent, we believe that the future belongs to a combination of these approaches or in other words to the "semiempirical" CS programs. The enrichment of the non-empirical programs by empirical selection criteria permitting a combination of the advantages of the exhaustive unbiased combinatorial sorting with a system of expert evaluations, developed as a result of the entire experience gained in organic chemistry, appears to be especially promising from this point of view.

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The High-temperature Corrosion of Constructional Ceramic Materials Based on Silicon Nitride

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The kinetics and mechanism of the processes taking place during the corrosion of ceramic materials based on silicon nitride in an atmosphere of oxygen, air, or fuel combustion products and under the influence of sodium salts have been examined. The influence of the composition and structure of the materials on their stability to oxidation has been demonstrated. The influence of corrosion on the physicomechanical properties of silicon nitride materials has also been examined. Methods of protection from corrosion, and the principles of the production of materials with a high heat resistance, have been described. The bibliography contains 138 references.

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I. INTRODUCTION

One of the most urgent problems in present-day technology concerns the production of ceramic materials suitable for manufacturing parts for gas turbine engines (GTE), heat exchangers, and other high-temperature equipment.[1-6]

The use of ceramic GTE makes it possible to increase the temperature of the gas at the outlet from the combustion chamber to 1400°, increase the efficiency, and decrease the fuel consumption.[4] The replacement of heat-resistant alloys by inexpensive ceramic in engine construction also leads to a sharp decrease in the consumption of scarce materials, such as tungsten, cobalt, and nickel, and to a decrease in the mass and cost of the engine.

In the solution of the problems of producing ceramic materials for engines, an important role is played not only by technologists, materials scientists, and strength specialists, but also by chemists. This is due to the fact that the constructional ceramic must have a high corrosion resistance in gaseous oxidising media. During use, the engine parts may be subjected to the action of atmospheric oxygen, fuel combustion products, and marine salts at temperatures up to 1500°.[7] The corrosion of the materials leads to a significant change in their physicomechanical properties, and may lead to breakdown of the entire ceramic construction, as took place, for example, during the testing of Ford's ceramic stator.[8]

The most promising constructional ceramic materials at present are those based on silicon nitride;[9-12] they are obtained by the following methods:

1) hot pressing in graphite or boron nitride press moulds at temperatures of 1700–1850° and pressures of 10–50 MPa;

2) isostatic hot pressing in static gas chambers under nitrogen pressures exceeding 100 MPa at temperatures up to 2000°;

3) activated sintering in furnaces at normal or slightly increased pressures; activation of the sintering usually requires the introduction of more than 10% of oxide additives into the materials;

4) reaction sintering of blanks of silicon or its mixtures with Si_3N_4, based on the reaction $Si + 2N_2 \rightarrow Si_3N_4$ at temperatures close to 1400°;

5) deposition from the gas phase, based on the reactions of silicon halides (SiF_4, $SiCl_4$, etc.) or silane SiH_4 with ammonia on heating.

Compact non-porous materials can be obtained by ordinary and isostatic hot pressing[9] and by deposition from the gas phase. The porosity of the specimens is usually 5–10% for activated sintering, and 15–30% for reaction sintering.[10]

Although thousands of papers and a number of fundamental monographs[13-17] have been devoted to the study of the high-temperature corrosion of metals, practically no attention was paid to the high-temperature corrosion of silicon nitride ceramics until 10–15 years ago. Although the first paper on the oxidation of Si_3N_4 appeared in 1959,[18] no significant progress was made in this field until the mid-seventies. Only an approach to this problem which was not directed towards the partial question of "the corrosion of Si_3N_4", but towards the complex problem of studying the corrosion of a whole class of materials, with allowance for the individual characteristic features of each material (method of preparation, concentration of impurities and additives, structure, etc.), made it possible to understand the mechanisms of the reactions taking place and to find ways of producing materials with a high corrosion resistance, capable of retaining sufficiently good mechanical properties at the temperatures at which they are used.

Extensive studies in the last ten years have examined the kinetics and mechanism of the corrosion of the ceramics at high temperatures in different media and the influence of corrosion on the crack resistance and other mechanical properties of ceramic materials, and ways of protecting them from active corrosion during use have been found. At the same time, there is little information on this topic in reference books and monographs giving data on the physicochemical properties of nitride ceramic materials.[19-27]

In the present work, an attempt has been made to summarise the progress made in the study of the corrosion of silicon nitride constructional ceramics and the production of materials with a high corrosion resistance at high temperatures.

II. THE THERMODYNAMICS, KINETICS, AND MECHANISM OF THE OXIDATION OF SILICON NITRIDE MATERIALS

Published data on the chemical reactions taking place during the oxidation of silicon nitride are contradictory. It has been suggested[18] that when it is heated in air to 1200°, silicon dioxide and nitrogen are formed by the reaction:

$$Si_3N_4+3O_2\rightarrow 3SiO_2+2N_2 \tag{1}$$

Other workers[28,29] detected silicon oxide nitride in the reaction products. This is believed to be formed by the reactions[28]

$$Si_3N_4+O_2\rightarrow Si_2N_2O+SiO(gas)+N_2$$
$$4Si_3N_4+3O_2\rightarrow 6Si_2N_2O+2N_2$$

In Ref.24, another reaction giving Si_2N_2O was proposed:

$$2Si_3N_4+3O_2\rightarrow 2SiO_2+2Si_2N_2O+2N_2$$

The oxide nitride in turn may be oxidised to SiO_2:[29]

$$2Si_2N_2O+3O_2\rightarrow 4SiO_2+2N_2 \tag{2}$$

A study of the oxidation of powdered Si_3N_4 under non-isothermal conditions[30] established that the oxide nitride is formed in the first stage of the process at temperatures up to 1100°. In the second stage (at temperatures of 1200° and above), Si_3N_4 and Si_2N_2O are oxidised to SiO_2 by reactions (1) and (2). At low partial pressures of oxygen, reactions giving gaseous silicon monoxide take place:[31,32]

$$Si_3N_4+3SiO_2\rightarrow 6SiO(gas)+2N_2 \tag{3}$$
$$2Si_3N_4+3O_2\rightarrow 6SiO(gas)+4N_2. \tag{4}$$

A thermodynamic calculation of the equilibria in the Si_3N_4–O_2 system (Fig.1) showed that, in addition to reactions (1)–(4), a whole series of other reactions giving solid (SiO_2, SiO) and gaseous (N_2, N_2O, NO, NO_2, SiO) products may take place:[24]

$$Si_3N_4+4O_2\rightarrow 3SiO_2+2N_2O \tag{5}$$
$$Si_3N_4+5O_2\rightarrow 3SiO_2+4NO \tag{6}$$
$$Si_3N_4+7O_2\rightarrow 3SiO_2+4NO_2 \tag{7}$$
$$2Si_3N_4+3O_2\rightarrow 6SiO(solid)+4N_2 \tag{8}$$
$$2Si_3N_4+7O_2\rightarrow 6SiO(solid)+8NO \tag{9}$$
$$2Si_3N_4+11O_2\rightarrow 6SiO(solid)+8NO_2 \tag{10}$$
$$2Si_3N_4+5O_2\rightarrow 6SiO(gas)+4N_2O \tag{11}$$
$$2Si_3N_4+7O_2\rightarrow 6SiO(gas)+8NO \tag{12}$$
$$2Si_3N_4+11O_2\rightarrow 6SiO(gas)+8NO_2 \tag{13}$$
$$Si_3N_4+O_2\rightarrow SiO_2+2SiN(gas)+N_2 \tag{14}$$
$$2Si_3N_4+O_2\rightarrow 2SiO(solid)+4SiN(gas)+2N_2 \tag{15}$$
$$2Si_3N_4+O_2\rightarrow 2SiO(gas)+4SiN(gas)+2N_2 \tag{16}$$
$$2Si_3N_4+O_2\rightarrow 6Si+2N_2O+2N_2 \tag{17}$$
$$Si_3N_4+2O_2\rightarrow 3Si+4NO \tag{18}$$
$$Si_3N_4+4O_2\rightarrow 3Si+4NO_2 \tag{19}$$

Fig.1 shows that the highest absolute values of the change in the Gibbs free energy correspond to the reactions giving silica. At both low and normal pressures, however, their thermodynamic probability decreases with increase in temperature.

To determine which of the possible reactions of Si_3N_4 oxidation is the main reaction, the gaseous products of the oxidation of Si_3N_4 were studied[33] by mass spectrometry. The species O_2^+, N_2^+, NO^+, N_2^{2+}, and O_2^{2+} were detected; SiO^+ ions could not be detected. It was concluded that the main reaction in the oxidation of Si_3N_4 in an atmosphere of air or oxygen (22.7 kPa) is reaction (6), and that the next stage of the process involves the high-temperature dissociation of **NO**:

$$2NO\rightarrow N_2+O_2$$

Infrared spectroscopy at an oxygen pressure of 10^5 Pa [34,35] detected nitrogen dioxide among the oxidation products.

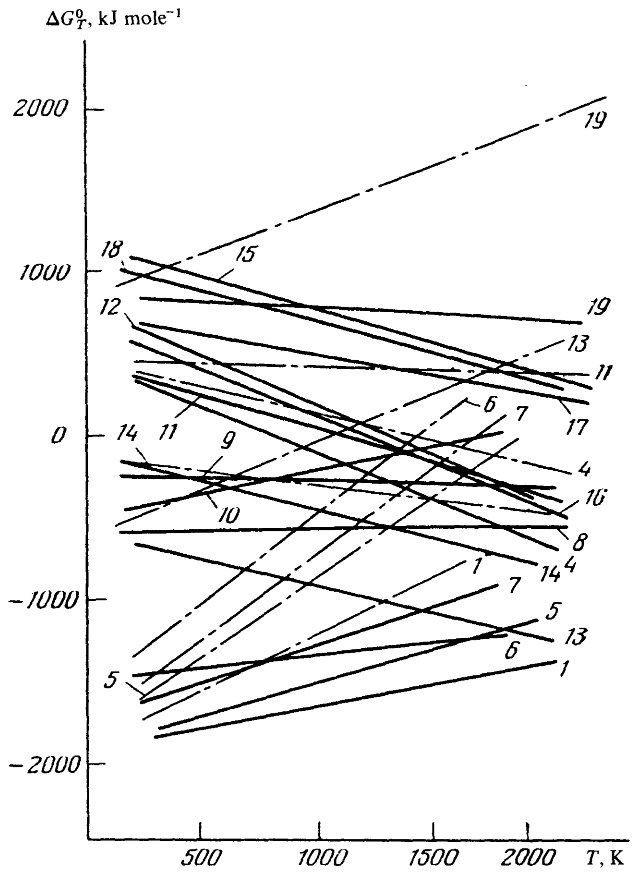

Figure 1. Dependence of the change in the Gibbs free energy ΔG^0_T on the temperature of the reaction of silicon nitride with oxygen at oxygen pressures of 10^5 Pa (continuous line) and 1.3×10^{-3} Pa (broken line) (the numbering corresponds to that of the equations for the reactions).[24]

In Ref.36 it was reported that reaction (3) can take place above 1500°. This suggestion was based on the fact that during the oxidation of the materials at high temperatures, the smooth surface of the specimens becomes blistered as a result of active gas liberation through the oxide film. It is also necessary to take account of the fact that at temperatures above 1420°, Si_3N_4 begins to dissociate to the elements, and the silicon formed reacts with SiO_2 to give gaseous silicon monoxide. It has been reported that the additives introduced into the material may have a catalytic influence on the processes taking place during the oxidation. Thus for example the addition of 5% NaF leads to the formation of silicon oxide nitride instead of SiO_2,[37] whereas the presence of magnesium facilitates the oxidation of Si_3N_4 to SiO_2.[38] The most desirable reactions are those giving silicon dioxide, since this facilitates the formation on the surface of the specimen of a protective layer which prevents further oxidation of the material.

At low partial pressures of oxygen, when only gaseous oxidation products are formed,[31,32] or under conditions in which the solid oxide layer formed on the surface does not show protective properties,[39,40] the rate of oxidation is independent of the time from the start of the process. In this case the following linear relationship is observed:

$$dx/d\tau = K_{\text{lin}} \text{ or } x = K_{\text{lin}}\tau + C_{\text{lin}}$$

where K_{lin} is the linear reaction rate constant, C_{lin} the constant of integration, τ the oxidation time, and x the relative change in mass on unit surface area of the specimen ($\Delta m/S$). The fact that the rate of oxidation remains constant with time indicates that the limiting stage of the process is the reaction at the phase interface.[13]

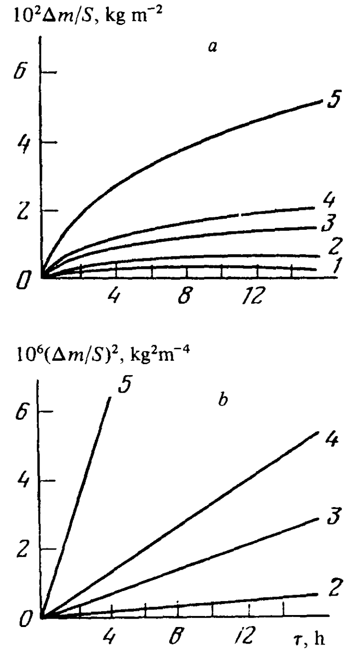

Figure 2. Kinetic curves for the oxidation of Norton's hot-pressed material HS-130 in oxygen, constructed on coordinates $\Delta m/S-\tau$ (*a*) and $(\Delta m/S)^2-\tau$ (*b*),[31] for different temperatures (°C): *1*) 1090, *2*) 1205, *3*) 1260, *4*) 1315, *5*) 1370.

In those cases where the surface of the specimen is covered by a compact oxide layer during oxidation, a parabolic time dependence is observed (Fig.2):

$$dx/d\tau = K'_{\text{par}}/x \text{ or } x^2 = K_{\text{par}}\tau + C_{\text{par}}$$

where K'_{par} and K_{par} are the parabolic reaction rate constants, and C_{par} the constant of integration. The fact that the parabolic oxidation law is observed indicates that the rate of the process is limited by diffusion through the oxide layer.[13] This process can be described by the theory of high-temperature oxidation proposed by Wagner,[41] according to which the rate of the overall reaction is determined by the bulk diffusion of the reacting ions or the corresponding point defects, or by electron transfer through the oxide layer. The driving force of the reaction is the change in the Gibbs free energy, associated with the formation of the oxide from the element and oxygen, as a result of which concentration gradients are produced in the oxidised layer. In this interpretation, the rate of growth of the oxide film is determined by the concentration gradients and the rates of diffusion of the components.

Wagner's theory is applicable to the oxidation of materials based on silicon nitride,[31] but the process is complicated by the fact that, in addition to solid products, gaseous oxidation products are formed; this makes a quantitative estimation and interpretation of the results difficult. The application of Wagner's theory with certain assumptions[42] made it possible to predict that oxidation leading to the formation of silicon monoxide by reactions (3) and (4) can take place, for example at 1300°, only if the oxygen pressure is less than 80 Pa.[31] The ranges corresponding to the "active" oxidation of Si_3N_4, when only gaseous products are formed, and to the "passive" oxidation, when solid products are formed, are shown in Fig.3 [43] (the first lies below the straight line, and the second above it). There is lack of agreement on which is the limiting stage in the oxidation when solid products are formed: diffusion of oxygen to the Si_3N_4/SiO_2 interface,[44] diffusion of nitrogen to the SiO_2/medium interface,[45] or diffusion of additives and impurities from inner layers towards the surface of the specimen.[46]

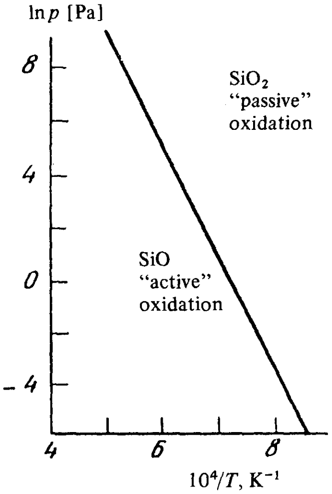

Figure 3. Dependence of the partial pressures of oxygen at which the change from "active" to "passive" oxidation takes place on the temperature of the process.[43]

Table 1 shows that the apparent activation energy of the oxidation of most forms of powdered and compact materials based on Si_3N_4 is close to 300 kJ mole^{-1}, that is it is close to the activation energy of the diffusion of oxygen in silicon dioxide. This indicates that the main contribution to the activation energy is made by the diffusion of oxygen through the oxide layer, and that this is the limiting stage of the process. The activation energy of the oxidation of silicon carbide is also close to 300 kJ mole^{-1} (see Table 1), since in this case also the rate of the process is limited by the diffusion of oxygen through the SiO_2 layer. At the same time, for some materials, the values of E show considerable deviations, towards both higher and lower values. In these cases the mechanism of the oxidation is apparently influenced considerably by other factors such as the diffusion of additives and impurities, transformations in the oxide layer, etc.

Table 1. Apparent activation energies (E) of the oxidation of various materials, and the activation energy of the diffusion of oxygen in silicon dioxide.

Material	Medium	t, °C	E, kJ mole^{-1}	Refs.
β-Si_3N_4 powder	air	1000—1100	280	[30]
β-Si_3N_4 powder	air	1200—1500	390	[30]
Si_3N_4 powder	dry air	1065—1340	285	[47]
Si_3N_4 powder	dry oxygen	1065—1340	255	[47]
α-Si_3N_4 powder	air	1150—1230	294	[48]
Reaction-sintered Si_3N_4	air	1100—1200	130	[49]
Reaction-sintered Si_3N_4	air	<1100	320	[49]
Hot-pressed Si_3N_4 + 1% MgO	dry oxygen	1000—1400	255	[31]
Hot-pressed Si_3N_4 + 1% MgO	moist oxygen	1200—1400	375	[50]
Hot-pressed Si_3N_4 + CeO_2 + SiO_2	air	1100—1370	350	[51]
Hot-pressed Si_3N_4 + 8% Y_2O_3 + 1% MgO	air	<1150	120	[46]
Hot-pressed Si_3N_4 + 8% Y_2O_3 + 1% MgO	air	1150—1350	580	[46]
Hot-pressed Si_3N_4 + 8% Y_2O_3 + 1% MgO	air	>1350	960	[46]
Hot-pressed $Si_{2.9}Be_{0.1}N_{3.8}O_{0.2}$	air	1400—1500	700	[52]
Pyrolytic Si_3N_4 (crystalline)	dry oxygen	1550—1650	390	[53]
Pyrolytic Si_3N_4 (amorphous)	dry oxygen	1550—1650	460	[53]
SiC powder	dry oxygen	1200—1500	277	[54]
Diffusion of oxygen in fused SiO_2	–	925—1225	298	[55]

In all cases except Ref.30, the apparent activation energy E was determined using the Arrhenius equation from the parabolic kinetic curves for the oxidation, obtained under isothermal conditions:

$$K_{\text{par}}=A\cdot e^{-E/RT}$$

where A is the pre-exponential factor, R the universal gas constant, and T the temperature. In Ref.30, E was found from the results of experiments under non-isothermal conditions at different heating rates using the equation

$$E=2{,}19R\frac{d\,(\lg\beta)}{d(1/T_p)}$$

where β is the heating rate, and T_p the temperature of the peak on the corresponding differential thermal analysis curve.

In those cases where the oxidation is accompanied by a continuous change in the area of the reaction surface as a result of the filling of the pores by the oxide phase formed, the change in the mass of the specimens with time may also be given by the logarithmic law:[56]

$$x=K_{\log}\lg\tau+C_{\log}$$

where $K_{\log}$ is the logarithmic rate constant, and $C_{\log}$ a constant. In the opinion of the authors of Ref.57, the kinetics of the oxidation of porous reactive silicon nitride can be described by Evans' equation for the case of self-blocking pores:

$$x=x_\infty(1-e^{-K\tau})$$

where x_∞ is the final increase in mass, corresponding to the horizontal section on the kinetic curve, and K a constant whose value depends on the time taken to reach this section. The use of various other familiar equations was also proposed. Analysis shows, however, that the kinetic curves for the isothermal oxidation of porous materials (Fig.4) cannot be accurately described by any of these equations throughout the range of temperatures (800–1500°) and times of treatment studied. This is due to the change in the mechanism of the process and the nature of the filling of the pores with increase in the temperature and time of oxidation.

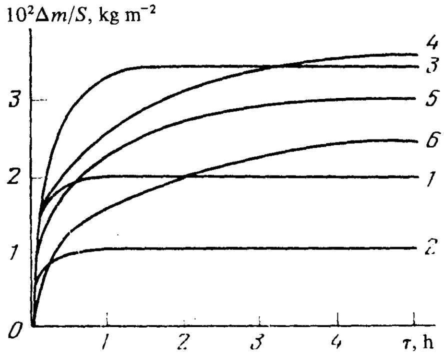

Figure 4. Kinetic curves for the oxidation of the reaction-sintered material NKKKM-80 in air[56] at different temperatures (°C): *1*) 1450, *2*) 1350, *3*) 1100, *4*) 1000, *5*) 900, *6*) 800.

Thus the mechanism of the oxidation may change with change in the conditions of the process (temperature, pressure, and other factors) and in the additives introduced into the ceramic, leading to changes in the composition of the oxidation products and the nature of the kinetic curves.

III. COMPOSITION AND STRUCTURE OF THE OXIDE LAYER

As shown in the previous section, the oxidation of silicon nitride materials in oxygen-containing media at a relatively high partial pressure of oxygen (see Fig.3) begins at temperatures above 700° and leads to the formation of a layer of silicon dioxide on the surface of the specimens.

At temperatures up to 1065°, the silicon dioxide formed is amorphous. At higher temperatures, in the opinion of many workers,[58,59] cristobalite is also formed. In Ref.56, both cristobalite and amorphous SiO_2 were detected throughout the temperature range from 800° to 1450°, but their quantitative ratio in the oxide layer was different for different oxidation temperatures. The appearance of cristobalite has also been observed in the oxidation of silicon oxide nitride.[60] In the oxidation of various materials, the formation of tridymite at temperatures above 1125° [47] and of quartz above 1385° [46] has been observed. There are no published data on the detection of other forms of SiO_2.

The phase transformations in silicon dioxide depend markedly on the temperature, rate of cooling, and presence of impurities.[61] These factors apparently determine whether the silicon dioxide formed in the oxidation is present in the amorphous state or as one of its crystalline forms. In addition to silicon dioxide, the surface layer of specimens oxidised in a charge of Si_3N_4 and other powders which actively absorb oxygen may also contain the oxide nitride.[62] The formation of Si_2N_2O was also detected in the oxidation of reaction-sintered silicon nitride at 1500° in a closed vessel made of a ceramic based on silicon nitride.[56] In a tubular furnace with free access of air, the formation of the oxide nitride could not be detected. It is therefore formed only when there is an oxygen deficit. In an excess of oxygen, the formation of SiO_2 is usually observed.

It has been reported[24] that at temperatures up to 900° in air, solid silicon monoxide may also be formed on the surface of the specimen as a brown phase with inclusions of bright-red crystals. This was not confirmed by other workers, however.[35,40,56] There are no reliable reports of the formation, between the SiO_2 and Si_3N_4 layers, of intermediate layers consisting of lower oxides or the oxide nitride, as observed in the oxidation of many metals[13] and metal-like refractory compounds.[24]

The surface oxide layer always contains impurities with a high affinity for oxygen, in quantities much greater than their average concentration in the bulk of the material. Thus according to Ref.31, after the oxidation of a specimen with the composition Si_3N_4 + 1% MgO at 1400° in dry oxygen, the protective film consists chiefly of enstatite $MgSiO_3$. The presence in the surface layer of up to 40% calcium at a calcium concentration of less than 1% in the starting material has been reported.[58] The migration of calcium, magnesium, and other impurity elements to the surface of the specimen leads to the formation of a silicate phase with a softening temperature in the range 1100–1300°.[38,63] The formation of a low-melting silicate phase, on the one hand, is beneficial, since it leads to the healing of cracks, pores, and other defects[64] and to a more uniform distribution of the oxidation products on the surface of the specimen. On the other hand, diffusion through the liquid layer takes place more readily, leading to an increase in the rate of oxidation. When a liquid phase is formed at the grain boundaries, the strength of the material decreases sharply.[65]

The dissolution of Si_3N_4 in the liquid oxide phase leads to an increase in its viscosity and to the formation of a vitreous coating on the surface of the specimens.[38] The addition of lanthanide oxides, and the presence of water vapour in the reaction atmosphere, on the other hand, favour crystallisation of the oxide layer.[50]

IV. INFLUENCE OF THE COMPOSITION AND STRUCTURE OF THE MATERIALS ON THEIR STABILITY TO OXIDATION

1. Influence of the Phase Composition

Silicon nitride exists in two polymorphic forms with similar structures, differing only in the sequence of tetrahedral elements in the direction of the c axis.[22] The nitriding of silicon usually gives both forms: α-Si_3N_4 is formed preferentially in the temperature range 1200–1400°, and β-Si_3N_4 above 1450°. On heating to 1450–1500°, slow irreversible conversion of the α-phase into the β-phase takes place.[21] Practically all industrial specimens of powdered silicon nitride consist of a mixture of the α- and β-forms.[66,67] At the same time, hot-pressed and sintered materials obtained at ~1700° and above usually do not contain α-Si_3N_4. Its presence is possible only in reaction-sintered materials.

The study of powders with different concentrations of α- and β-Si_3N_4 [24] has shown that, other conditions being equal, the tendency to undergo oxidation is greater for those consisting chiefly of α-Si_3N_4. The initial rate of the process increases with increase in the oxygen pressure, indicating the possible adsorption of molecular oxygen. At certain temperatures and partial pressures of oxygen, a solid solution of O_2 in α-Si_3N_4 is formed.[24] With increase in the oxidation temperature, the concentration of α-Si_3N_4 in specimens of reaction-sintered Si_3N_4 also decreases.[28] This apparently takes place as a result of the preferential oxidation of the α-phase. The lower stability of α-Si_3N_4 to oxidation may be due to its instability at high temperatures. The rearrangement of the crystal lattice of α-Si_3N_4 facilitates the addition of oxygen atoms and oxidation of the material.

Deposition from the gas phase may give not only crystalline but also amorphous silicon nitride,[12,53] which has a higher stability to oxidation than the crystalline forms.[53]

2. Influence of Porosity

The oxidation of specimens of hot-pressed Si_3N_4, having a density close to the theoretical, takes place chiefly on the surface. The resulting surface oxide layer, depending on the oxidation temperature, the chemical composition of the material, and the oxidising medium, may be porous or compact, crystalline or amorphous.[31,68–71] Typical kinetic curves for the oxidation of compact hot-pressed Si_3N_4,[31] obeying a parabolic time dependence, are given in Fig.2.

The oxidation of specimens of reaction-sintered silicon nitride, having the usual porosity of 15–30%,[72–75] take place throughout the entire volume (the corresponding kinetic curves are given in Fig.4). The rate of oxidation of porous specimens is much higher than that of the compact materials. The difference is particularly marked at relatively low temperatures (compare Figs.2 and 4). As a result of the oxidation of reaction-sintered Si_3N_4 with a porosity of 2270 kg m^{-3} at 1040° for 200 h, 28% SiO_2 accumulated in the specimen, whereas its concentration in the original material (as an impurity at the grain boundaries) did not exceed 4%.[72]

According to Ref.76, the dependence of the rate of oxidation on the porosity is linear and is given by the equation

$$\Delta m = kS_0 + 3kf(1-\rho)/\bar{R}$$

where Δm is the increase in mass, S_0 the geometric surface area of the specimen, f the fraction of open pores (relative to the total porosity), $\bar{R}$ the average radius of the pores, ρ the relative density of the material, and k a coefficient. This equation shows that an important role is played not only by the total fraction of open pores, but also by the radius of the pores (see also Fig.5). In Ref.77 it was suggested that the main influence on the stability to oxidation is in fact shown not by the radius of the pores but by the radius of the channels connecting them. The filling of these channels by an oxide phase having a greater volume than the original Si_3N_4 leads to a decrease in the rate of internal oxidation of the material. Thus for materials with a smaller average radius of the pores (or of the channels connecting the large pores), the formation of a protective layer on the surface of the specimens takes place more rapidly at a lower degree of oxidation (Fig.5).

Active oxidation of the specimen throughout its volume takes place under conditions in which a solid oxide layer exists on its surface. This corresponds to curves *4–6* in Fig.4. When the oxide phase melts (see section III), a viscous protective film, covering all the open pores, is formed after a certain time interval on the surface of the specimens, leading to a change in the nature of the kinetic curves with increase in the oxidation temperature (curves *1–3* in Fig.4).

In the oxidation of the porous material, its density increases,[78] and the porosity decreases, whereas in the oxidation of hot-pressed Si_3N_4 there is a slight decrease in the density. This last feature is due to the fact that the silicon dixode formed is less dense than Si_3N_4. In the oxidation of the compact material, the SiO_2 layer is formed only on the surface, whereas in the oxidation of a porous specimen, only ~25% of the silicon dioxide formed corresponds to the surface layer,[59] and the slight change in the volume of the specimen is accompanied by a fairly large change in its mass.

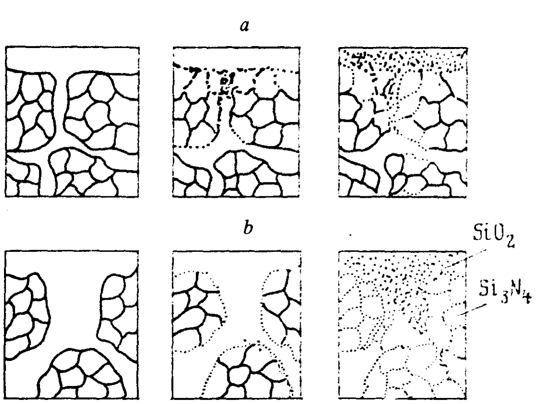

Figure 5. Model of the oxidation of reaction-sintered silicon nitride with fine (*a*) and coarse (*b*) pores under the conditions of formation of a solid oxide layer.

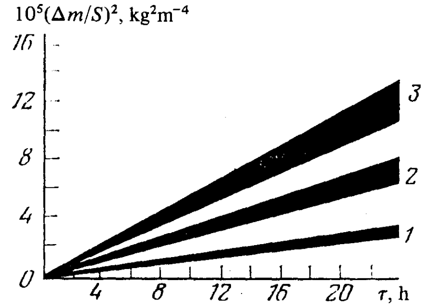

Figure 6. Kinetics of the oxidation of the material HS-130 at 1400° in different media:[81] *1)* CO/CO_2, $p_{total} = 2 \times 10^4$ Pa, $p_{O_2} = 10^{-4}$–10^{-1} Pa; *2)* O_2, $p_{total} = p_{O_2} = 8 \times 10^2$–$8 \times 10^4$ Pa; *3)* O_2/N_2, O_2/Ar, $p_{total} = 8 \times 10^4$ Pa, $p_{O_2} = 8 \times 10^2$–8×10^4 Pa.

Even at temperatures below 1000°, oxidation leads to gradual covering of the pores (Fig.6), and, after some time, to the formation of a protective film of silica on the surface of the specimen, which stops practically completely the penetration of oxygen into the inner layers of the material. Under these conditions, the diffusion of oxygen through the layer of oxide becomes the limiting stage of the process. Subsequently, the reaction takes place in the same way as in the oxidation of the non-porous hot-pressed material.

The density and behaviour during oxidation of sintered materials having a porosity of ~10%[79] are intermediate between those of the hot-pressed and reaction-sintered materials. The materials obtained by deposition from the gas phase have a high density. Their properties are closer to those of the hot-pressed materials,[53] and their mechanical properties and stability to oxidation are often even greater than those of these materials.

3. Influence of Additives and Impurities

Practically all materials based on silicon nitride contain additives to activate sintering: MgO,[80,81] Al_2O_3,[82] Y_2O_3,[83] BeO,[52] CeO_2,[51] ZrO_2,[58] etc. The most frequently used additive is magnesium oxide. The best compaction is achieved when a secondary phase with the composition $MgSiN_2$—Mg_2SiO_4 is formed between the granules.[80] After the oxidation of these materials, the surface layer contains enstatite $MgSiO_3$ and forsterite Mg_2SiO_4,[79] formed by the reactions:

$$2MgO+SiO_2 \rightarrow Mg_2SiO_4$$

$$Mg_2SiO_4+SiO_2 \rightarrow 2MgSiO_3$$

The rate of oxidation increases with increase in the quantity of MgO added. This is due to the fact that the vitreous magnesium silicate phase formed at the grain boundaries softens at temperatures above 1100°, and its viscosity and melting point decrease with increase in the concentration of magnesium in it.[84]

The stability of materials of this type towards oxidation can be increased by adding zirconium dioxide in addition to magnesium oxide.[58] The hot-pressed material containing 1% MgO and 2% ZrO_2 has a much higher stability towards high-temperature oxidation than the same material without zirconium dioxide. It is considered[58] that the addition of ZrO_2 decreases the rate of the diffusion of oxygen through the oxide film and the transfer of magnesium ions to the surface of the specimen. Materials containing added ZrO_2 or ZrC have a high stability at temperatures up to 1500°.

The addition of yttrium oxide makes it possible to obtain a crystalline phase at the grain boundaries, and not the vitreous phase obtained when MgO is used, and also increases the high-temperature strength of the materials.[83] The silicon yttrium oxide nitrides formed by the reaction of Y_2O_3 with Si_3N_4 and SiO_2, which is always present on the surface of the silicon nitride granules, have been studied in detail.[85] It is recommended that the technological conditions be selected in such a way that the secondary phase consists of $Y_4Si_2O_7N_2$. This is facilitated by adding aluminium and magnesium oxides. This material has the greatest stability to oxidation. According to other data,[39] material from the Si_3N_4—$Y_2Si_2O_7$—Si_2ON_2 system has a very high resistance to oxidation.

Cerium oxide has approximately the same influence as yttrium oxide on the properties of the materials.[51] Materials containing added CeO_2 and Y_2O_3 have a high resistance to oxidation at 1300—1400°.[86] In the temperature range 900 to 1200°, the crystalline oxide film formed on the surface of the specimens does not show protective properties, so that intensive oxidation of the materials with a deterioration in their mechanical properties takes place.[40] It has been suggested[39,40] that the temperature separating these two ranges be called the critical temperature (T_C). Above T_C, the oxide layer is compact and shows good protective properties; the kinetics of the oxidation obey a parabolic law, and the rate of oxidation decreases with decrease in the concentration of the additive. Below T_C, the surface layer contains connected pores, and therefore has poor protective properties; the kinetics of the oxidation are close to linear. For the materials of the Si_3N_4—Y_2O_3 system studied in Ref.40, T_C = 1200—1250°. At a temperature below T_C, the maximum rate of oxidation is reached at 1000°.

The formation of a non-porous oxide layer requires that the material contain compounds which lower the liquidus temperature of the phase between the granules. One such compound is Al_2O_3. The addition of 2% aluminium oxide decreases the rate of crystallisation of the phase between the granules, facilitating glass formation, and lowers T_C by 200 K.[40] This material retains an acceptable strength only up to 1200°, but unlike materials to which only Y_2O_3 has been added, it shows good resistance to oxidation at 1000°, since this temperature is only slightly below its T_C value. A hot-pressed material consisting of 93% Si_3N_4, 5% Y_2O_3, and 2% Al_2O_3 showed good resistance in tests involving prolonged oxidation (up to 30 d) at 1200°.[69] The production of a hot-pressed material containing 8% Y_2O_3, whose properties did not deteriorate at 1000—1200°, has been reported.[68] The addition of aluminium oxide to silicon nitride gives so-called sialons,[87,88] which consist of a solid solution with the β-Si_3N_4 lattice, in which some of the silicon atoms are replaced by aluminium atoms, and some of the nitrogen atoms by oxygen atoms. Similar solid solutions are formed when the oxides of beryllium and various other elements are added.

Materials containing added beryllium oxide[52,89] also have a high resistance to oxidation. It has been reported[52] that a hot-pressed material with the composition $Si_{2.9}Be_{0.1}N_{3.8}O_{0.2}$ has a much greater heat resistance than industrial materials being produced. The activation energy of the oxidation of this material is almost twice that for most other silicon nitride specimens (see Table 1).

When the original powders are ground, they usually contain iron or tungsten carbide as impurities, depending on the material used to prepare the grinding bodies and the mill lining. Iron oxides in quantities up to 2.5% are sometimes added deliberately to reaction-sintered materials to facilitate the nitriding process.[90] After pressing or reaction sintering, these impurities are present in the prepared material at the grain boundaries either in the original state or as melts of the silicides or a mixed carbide of iron and tungsten.[38,90] At a high oxygen concentration, they are oxidised and dissolve in the intergranular phase, lowering its melting point. This leads to the formation of a liquid phase in the surface phase at high temperatures and to a deterioration in the high-temperature strength.[91,92]

In addition to the above elements, the technical raw material used to prepare most materials also contains traces of calcium, magnesium, aluminium, strontium, nickel, cobalt, manganese, copper, titanium, and other elements in quantities of 1.00 to 0.01%.[65,98] The presence of these elements in the material leads to a decrease in the viscosity of the silicate glass. The decrease in the viscosity is greater, the greater the ionic radius of the element and the higher the rate of oxidation. The oxidation resistance of the material HS-130, produced by the American firm Norton (Fig.2), is 10 times that of the similar material HS-110 in which the concentration of impurities is 10 times higher.[94] After oxidation, the impurities are present in the vitreous phase or separate as different crystalline phases.[95]

Thus additives and impurities which lower the melting point of the oxide phase may play a beneficial role, facilitating the formation of a compact protective layer even at temperatures of ~1000°. At the same time, at higher temperatures, they lead to a sharp increase in the rate of oxidation of the material. To produce heat-resistant materials, it is apparently necessary to remove the original impurities from the raw material, and then to introduce a strictly limited quantity of certain additives which give the material the required properties.

V. CORROSION UNDER THE INFLUENCE OF SALTS

During use, the ceramic parts of engines may be subjected to the action of various salts,[7,96] leading to breakdown of the protective oxide layer[97] and to more active corrosion of the material.

The presence of sodium salts in the surface layer leads to a decrease in the viscosity of the oxide phase and to an increase in the rate of oxidation of the specimens.[49] The oxide layer formed on the surface of specimens impregnated before oxidation with solutions of different sodium salts contain many pores and cracks.[98] The cracking of the surface layer is due to the difference in the coefficients of thermal expansion of the material and the sodium silicate glass formed, and the large number of pores is due to the low viscosity of the latter.

It has been reported that materials based on silicon nitride have a high stability to the action of molten NaCl,[98,99] marine salt,[98,100] and LiCl–KCl and LiF–LiCl–KCl mixtures,[101] but that they have a poor corrosion resistance in melts with strong oxidising properties, such as Na_2SO_4 [98] and the eutectics Na_2SO_4–NaCl [99] and Na_2SO_4–V_2O_5.[102] The reaction of silicon nitride with sodium sulphate gives the silicates Na_2SiO_3 and $Na_2Si_2O_5$. The processes taking place during corrosion in an Na_2SO_4 melt can be described as follows. In the temperature range 800–900°, the surface layer of the material is oxidised by atmospheric oxygen according to Eqn.(1). When the salt melts (at 890°), it begins to react with the silicon dioxide formed

$$2SiO_2+2Na_2SO_4\rightarrow 2Na_2SiO_3+2SO_2+O_2$$

leading to its dissolution. After the SiO_2 layer has dissolved, the salt reacts with Si_3N_4:

$$6Na_2SO_4+2Si_3N_4+3O_2\rightarrow 6Na_2SiO_3+4N_2+6SO_2$$

Silicon nitride materials have a higher resistance to the action of molten Na_2SO_4 than silicon carbide materials.[99]

VI. CORROSION IN DIFFERENT GASEOUS MEDIA

According to Ref.18, the rate of oxidation of silicon nitride in moist air is twice that in dry air. The reaction of Si_3N_4 with water vapour gives ammonia:

$$Si_3N_4+6H_2O\rightarrow 3SiO_2+4NH_3$$

At the same time, in other studies,[50] even mass spectrometry did not detect ammonia in the products of the reaction of Si_3N_4 with moist air (the partial pressure of water vapour was 3.3×10^3 Pa). The activation energy of the oxidation of hot-pressed silicon nitride in moist oxygen is greater than that in dry oxygen (see Table 1). This is attributed to the change in the viscosity of the oxide film as a result of the dissolution and diffusion of OH^- ions in it.[50]

At high temperatures, silicon nitride materials have a greater resistance in CO–CO_2 mixtures containing oxygen at a partial pressure of 10^{-4}–10^{-1} Pa, compared with an atomosphere of oxygen or air.[81] The shaded areas in Fig.6 give the ranges corresponding to the kinetic curves for the oxidation of hot-pressed silicon nitride in oxygen, CO–CO_2, and mixtures of oxygen with argon and nitrogen. At an oxygen pressure of 1.33 Pa in the CO–CO_2 mixture, a mass loss is even observed, due to the formation of gaseous silicon monoxide. The rate of oxidation of Si_3N_4 is independent of the partial pressure of nitrogen in the gas mixture.[31] Hydrogen also has no significant influence on silicon nitride.[18] Heating powdered Si_3N_4 in a stream of chlorine for 1 h at 1200° leads to an increase in mass of 1%.[18]

Silicon nitride ceramic has a high resistance to corrosion under the influence of the products of the combustion of high-quality fuel.[102] If however these products contain sodium and vanadium, even at concentrations of 0.005%, very strong corrosion of the material is observed. After 225 h at a temperature of 900–1100°, an oxide layer with a thickness of ~1 mm, containing up to 75% SiO_2, 7% V_2O_5, and 8% Na_2O, is formed on the surface of specimens of reaction-sintered silicon nitride.[102]

In spite of the limited amount of available data, it may be concluded that silicon nitride materials can be used successfully in atmospheres of dry nitrogen, hydrogen, chlorine, oxides of carbon, and also fuel combustion products at temperatures above 1000°. The working atmosphere, however, should not contain moisture or elements such as sodium, vanadium, etc. which lead to modification of the protective oxide layer on the surface of the material and to an increase in the rate of corrosion.

VII. THE INFLUENCE OF OXIDATION ON THE PROPERTIES OF THE MATERIALS

Oxidation has a marked influence on most physicomechanical properties of a material. A particularly important role is played by the internal oxidation of porous materials, but at high degrees of oxidation there is a marked change in the properties of even compact hot-pressed materials. Thus when reaction-sintered and hot-pressed silicon nitride is used in an oxidising medium at high temperatures, the influence of oxidation cannot be neglected, and must be taken into account when predicting the properties of the materials.

The increase in the concentration of SiO_2 in the material on oxidation leads to an increase in the coefficient of thermal expansion.[57] As a result of the increase in volume when Si_3N_4 is converted into SiO_2 and the difference in the coefficients of thermal expansion of the material and the oxide phase, compression stresses are produced in the surface layers of the specimens, leading to an increase in the strength of the material. When the stresses are too high, however, cracking of the surface layer takes place, with deterioration in the properties of the material.[103] Compression stresses are produced in the surface layer during the oxidation of the hot-pressed material containing added ZrO_2 even at temperatures of 600–800°.[104] This is due to the fact that it contains a secondary phase with the composition $ZrO_{2-2x}N_{4x/3}$ ($0.25\leqslant x\leqslant 0.43$), which at temperatures above 500° is oxidised to give monoclinic ZrO_2, with an increase in volume by 45%. At the temperatures at which the process takes place, neither Si_3N_4 nor Si_2N_2O are oxidised. Since the material is compact, the oxidation of the secondary phase takes place only on the surface. The compression stresses produced increase the strength, preventing the production of cracks in the surface layer.

Published data on the influence of oxidation on the strength of the materials are contradictory. According to some authors,[72,105] oxidation leads to a decrease in the bending strength, the strength decreasing to a greater extent with increase in the time of treatment. According to other data,[106,107] oxidation leads to an increase in the strength of the specimens as a result of the healing of surface defects. It is reported[107] that although oxidation increases the strength of the material in the initial period, increase in the time of treatment at 1200° to 100 h leads to a decrease in the strength of hot-pressed Si_3N_4 as a result of etching of the grain boundaries and the formation, along the boundaries, of grooves which act as stress concentrators and which may develop into cracks when a load is applied. At the same time it has been reported[108,109] that increase in the treatment time from 5 to 100 h does not lead to a change in the strength of reaction-bonded silicon nitride, irrespective of the temperature of testing (Fig.7). Treatment of specimens of reaction-bonded Si_3N_4 in air for 24 h at 1400° leads to an increase in its high-temperature strength.[26]

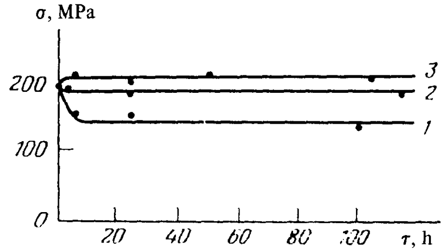

Figure 7. Dependence of the tensile strength of reaction-sintered silicon nitride at 20° on the time of treatment in air[108] at different temperatures (°C): *1*) 1400, *2*) 1200, *3*) 1000.

The bending strength of reaction-bonded and hot-pressed specimens of silicon nitride after oxidation at 1370° with and without an applied load was studied in Ref.105. During oxidation without the load, the strength of the reaction-sintered material increased, but that of the hot-pressed material decreased as a result of the growth of the nitride granules.

All the above data related to the strength determined in bending tests. In Ref.110 it was shown that the changes in the surface of the specimens produced by oxidation, as a result of the non-uniform distribution of the stresses, have a greater influence on bending than on elongation.

According to data obtained by the AiResearch Manufacturing Co., treatment for 50 h in air at 980° leads to an increase in the strength of hot-pressed silicon nitride. Turbine rotor blades produced by the firm were subjected to this treatment. The reaction-sintered materials were subjected to treatment for 2 h at 1400° or for 1 h at 1460°, followed by slow cooling in the furnace to room temperature.

Internal oxidation leads to a sharp deterioration in the creep resistance of the material.[77] Materials based on Si_3N_4 show good creep resistance at high temperatures in protective and reducing media. On heating in air or in oxygen, however, a silicate phase is formed as a result of oxidation of the material along the grain boundaries, leading to an increase in creep.

The influence of various changes taking place in the structure of materials during oxidation on their mechanical properties at room temperature and high temperatures has been analysed.[111-115] Some of the processes taking place during oxidation lead to an increase in the strength, crack resistance, and creep resistance (healing of defects, removal of impurities from the inner layers of the material, etc.), whereas others lead to a deterioration in the mechanical properties (cracking of the oxide layer, etching of the grain boundaries, etc.).[113] By selecting definite oxidation conditions depending on the structure and composition of the material, it is possible to achieve an increase in its strength and other mechanical characteristics. Extensive oxidation of a material leads to a deterioration in the mechanical characteristics; this is usually observed in the oxidation of porous specimens or during oxidation under conditions in which the oxide layer formed does not exhibit protective properties. It is therefore necessary to protect materials from active oxidation.

VIII. THE EFFECT OF SALTS ON THE STRENGTH AND CRACK RESISTANCE OF THE CERAMIC

Oxidation in the presence of sodium salts leads to a decrease in the strength and the critical stress intensity factors (Table 2), both at room temperature and at 1200°.[98] The decrease in strength at high temperatures is due to the formation of a liquid silicate phase in the surface layers of the material, and the decrease at room temperature is due to cracking of the oxide layer (see section V). The higher the oxidation temperature, the lower the strength of the specimens at room temperature.

Table 2. The influence of salts on the strength and crack resistance of the reaction-sintered material NKKKM-81.[98]

Form of treatment	T = 20°		T = 1200°	
	σ_b, MPa	K_{I_c}, MN m$^{-3/2}$	σ_b, MPa	K_{I_c}, MN m$^{-3/2}$
Without treatment	207	3,21	177	3.19
Corrosion in an NaCl melt at 950° (1 h)	195	3.14	128	2.83
Oxidation at 1200° (15 min) in the presence of NaCl	163	—	131	2,71
Oxidation at 1200° (15 min) in the presence of marine salt	157	—	110	2.57
Oxidation at 1200° (15 min) in the presence of Na_2SO_4	177	—	93	2.38

Notation: T is the temperature at which the tests were carried out, σ_b the bending strength, and K_{I_c} the critical stress intensity factor.

Table 2 shows that corrosion in melts of marine salt, sodium chloride, and the NaCl–Na_2SO_4 eutectic leads to a deterioration in all the mechanical characteristics of the materials at all temperatures of testing.[98,116,117] Increase in the time of treatment in molten NaCl from 1 h to 5 h, however, does not lead to a further decrease in strength.[98] Molten salts which have a stronger corrosive action on the material lead to a marked decrease in strength. This is due to the formation of defects in the surface layer of the specimens as a result of the corrosion breakdown of the grain boundaries and individual phase components of the material.[98,116]

In spite of the fact that corrosion under the influence of salts leads to considerable deterioration in the properties of silicon nitride materials, there is very little published information on methods of protection from "salt" corrosion.

IX. CORROSION UNDER STRESS

It is well known that the simultaneous action of a corrosive medium and mechanical loading on metals,[118] glass,[119] molecular crystals,[120] plastics,[121] and other materials leads to so-called corrosion under stress or to corrosion cracking. Since only the first steps are now being taken in the use of ceramics as constructional materials, the corrosion of silicon nitride ceramic under stress has been little studied.

The authors of Ref.122 consider that materials based on Si_3N_4 do not undergo corrosion under stress. This conclusion was based on the following factors: 1) the energy of thermal activation of the process is much higher than the typical energy for a chemical reaction; 2) attempts to stimulate the growth of a crack at the temperature of the surrounding medium in the presence of corrosive agents were unsuccessful; and 3) in the study of corrosion under stress at high temperatures, cracks produced artificially showed a tendency to close. At the same time, it has been reported[123,124] that reaction-sintered and hot-pressed silicon nitride specimens are sensitive to corrosion under the influence of stresses in moist air, water vapour, and aqueous media at temperatures up to 300°. The lower the pH of the medium, the lower the strength of the specimens. The authors of Ref.123 consider that the corrosion of silicon nitride materials under stress is due to ion exchange between the medium and a vitreous phase between the granules. Since practically all materials based on Si_3N_4 contain a secondary vitreous phase, they should be sensitive to corrosion under stress to the extent that the glasses and their breakdown can be described by the theory developed for glasses by Charles and Hillig.[125]

The influence of the external medium may also be due to the dependence of the time to breakdown on the magnitude of the applied load, observed in static fatigue tests on silicon nitride materials.[126,127] When a reaction-sintered ceramic based on silicon nitride was tested in air at temperatures close to 800°, a marked deterioration in the strength properties, which depended on the time of treatment under load, was detected. In this case, not only did the chemical reaction with the medium influence the mechanical properties, but the mechanical stresses also influenced the oxidation process. The quantity of cristobalite in the specimens after testing increased with increase in the applied load.[128] The information available at present, however, does not make it possible to determine reliably the mechanism of the breakdown of silicon nitride ceramic under the influence of mechanical stresses in a corrosive medium.

X. THE PROTECTION OF THE MATERIALS FROM OXIDATION

Various methods of protection from oxidation have been described. The chief method for protecting the ceramic is by depositing coatings of nitrides, carbides, or oxides on its surface.[129–131] Silicon nitride and carbide obtained by deposition from the gas phase have a very high resistance to oxidation. Oxide coatings can also provide reliable protection for the materials. The optimum work capacity of articles with coatings is achieved by depositing silicon nitride, since this ensures good adhesion to the support and a decrease in the possibility of separation or cracking of the coating when heated as a result of a difference in the temperature coefficients of linear expansion of the support and the coating.[25] The principal methods used to apply coatings are by deposition from the gas phase[129,130] and by plasma spraying.[131,132]

The reactions of silicon halides or silane with ammonia are widely used to obtain protective coatings of silicon nitride. The method of pyrolytic deposition with controlled nucleus formation[133] makes it possible to obtain fine-granular coatings consisting of equiaxial crystals. The deposition of a fine-granular coating with a thickness of 0.05 mm and granule dimensions of 1–10 μm on the surface of specimens of reaction-sintered silicon nitride increases the resistance of the material to oxidation during cyclic heating to 1200° by a factor of 100.[133] To give the ceramic other special properties in addition to corrosion resistance (erosion resistance, hardness, etc.), it is also possible to deposit composite coatings with a matrix of amorphous Si_3N_4 and inclusions of TiN, BN, and other compounds.[134]

Coatings of silicon carbide are obtained by the gas-phase synthesis of SiC from volatile silicon halides and hydrocarbons.[135] The deposition of a coating of pyrolytic silicon carbide on the surface of the material by the decomposition of trichloromethylsilane in a tubular furnace at 920° has been proposed.[75,136] The material with a porosity of 25%, covered with a layer of SiC, had an absolute creep resistance at 1200°, indicating the absence of internal oxidation. Coatings of titanium and zirconium diborides and aluminium nitride can also be applied.[133]

Good results were obtained when specimens with a porosity of 28% were impregnated with liquid silicon in a nitrogen atmosphere.[137] After this treatment, a compact protective layer with a thickness of 40–100 μm was formed on the surface of the specimens. An interesting feature is that this layer consisted entirely of β-Si_3N_4, which is known to be extremely stable to oxidation, whereas its concentration in the specimen did not exceed 4%. The increase in the mass of specimens with a coating thickness of 45 μm during their oxidation in the temperature range 800–1400° was one tenth of that for the non-protected specimens. For specimens with a film thickness of 100 μm, practically no increase in mass was observed up to 1400°. The specimens showed a high resistance to oxidation in moist air at 1400°, whereas under similar conditions the non-protected specimens were oxidised to the extent of 30%. In practice, however, the use of this method of protection encounters considerable difficulties, associated with the need for thorough removal of oxygen-containing silicon compounds from the surface, since Si_3N_4 containing SiO_2 or Si_2N_2O on its surface is not wetted by liquid silicon.

According to data given by Norton, reaction-sintered materials can be protected from oxidation by treating with solutions of $Al(NO_3)_3$, $ZrOCl_2$, organometallic compounds of zirconium, or a mixture of $ZrOCl_2$ and $Y(NO_3)_3$. After repeated impregnation, the specimens are heated in a nitrogen atmosphere; the decomposition products collect and fill the pores on the surface of the specimens. The strength of the materials remains unchanged after this treatment, but if materials to which zirconium compounds have been added are heated for 50 h in air at 1230°, their bending strength increases considerably.

Impregnating porous reaction-sintered materials with organosilicon compounds followed by their thermal decomposition makes it possible to increase the resistance of the materials not only to oxidation but also to corrosion under the influence of salts.[138]

The processes described above are not always easy to carry out from the technological viewpoint. A much simpler method of protection is by preliminary oxidation of the specimens under appropriate conditions. As already noted, to obtain useful materials it is necessary to create conditions favouring the formation on the surface of the articles (during use in an oxidising medium at high temperatures) of a compact protective oxide layer. In a certain temperature range (for most materials at temperatures close to 1000°), however, the rate of oxidation is already fairly high, but a protective layer has not yet been formed. This is particularly dangerous for porous materials, since it may lead to their extensive internal oxidation. To eliminate undesirable phenomena, it has been proposed that a compact oxide layer be produced artificially on the surface of reaction-sintered materials by placing them for a short time in a furnace heated to 1300 to 1350°.[56] Thermal treatment in this way is used by the AiResearch Manufacturing Co. to protect materials from further oxidation during use, with a simultaneous increase in their strength.

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Thus oxidation during use represents a serious danger for silicon nitride materials, since it may lead to a marked deterioration in their mechanical characteristics. This applies particularly to porous reaction-sintered ceramic. At the same time, a knowledge of the regular features of the process makes it possible, by using definite oxidation conditions, to achieve an increase in the strength of the materials and to protect them from active oxidation during subsequent use. Here it is necessary to take account of the fact that the materials described in the present review differ considerably in their behaviour in oxidising media at high temperatures, depending on their composition and structure.

Although much of the published material on the oxidation of silicon nitride ceramic is contradictory, the principal regular features of this process have now been established. At the same time, however, corrosion under the influence of salts and in an atmosphere of fuel combustion products has still been insufficiently studied. In addition, the conditions under which a ceramic based on silicon nitride undergoes corrosion under the influence of stresses have not yet been established. To ensure that the materials can function at high temperatures in media containing salts of sodium and other metals, a more detailed study of the corrosion processes using modern methods of physicochemical analysis is necessary.

Although silicon nitride materials may undergo considerable corrosion in the media described above at temperatures higher than 1000°, with a deterioration in their mechanical properties, they nevertheless retain under these conditions a higher strength than other heat-resistant and corrosion-resistant metallic alloys.

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Organophosphorus Compounds in Reactions with Quinones

A.A.Kutyrev and V.V.Moskva

The results of studies on the chemical behaviour of organophosphorus compounds in reactions with quinones are surveyed. Attention is concentrated on discovering the trends and general characteristics of such processes.
The bibliography includes 134 references.

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I. INTRODUCTION

During the last quarter of a century, studies in the chemistry and technology of organophosphorus compounds have expanded greatly throughout the world, in many respects due to the growing needs for biologically active preparations, among which the aromatic esters of phosphorus acids play a leading role.

Until recently, there has been no reliable information about the reaction mechanisms and frequently also about the structure of the products of the interaction of organophosphorus compounds with quinones. Only the wide-scale application of modern physical research methods made it possible to solve some of these problems.[1-4] Nevertheless, a number of processes with participation of phosphorus(III) compounds do not fit within the framework of existing ideas[5] and the reactivities of compounds of pentacoordinate phosphorus in relation to quinones are not susceptible to prediction.

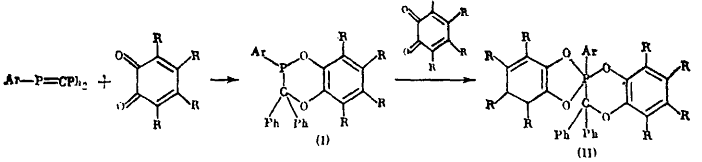
There are no publications in the literature of a review character on the interactions of phosphorus compounds with quinones. The monographs and reviews devoted to various aspects of the chemistry of organophosphorus compounds[6-10, 13,14] and quinonoid compounds[4,11,12] provide only disjointed descriptions of individual phosphorus-containing reagents in their reactions with certain quinones.

In the present review an attempt has been made to survey the experimental data on the synthesis, reactivities, and mechanisms of the reactions of organophosphorus compounds with quinones. The aim was not to discuss comprehensively all the reactions described in the literature but an attempt has been made to concentrate attention on the general characteristic features of these chemical reactions.

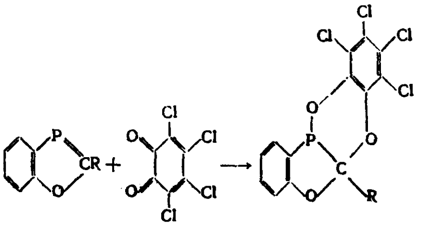
II. COMPOUNDS OF DICOORDINATE AND TRICOORDINATE PHOSPHORUS

1. Reactions of Phosphines and Related Compounds with Quinones

The study of the interaction of aryldiphenylmethylenephosphine with tetrachloro-1,2-benzoquinone, 3,5-di(t-butyl)-1,2-benzoquinone, and phenanthrenequinone showed that 1:1 cyclic [2+4] adducts (I) are formed in all cases. For a 1:2 ratio of phospha-alkenes and quinones, the main reaction products are phosphoranes (II):[15]



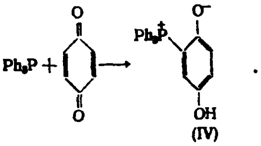
1,3-Benzoxaphosphole reacts with tetrachloro-1,2-benzoquinone to form the phosphinite (III):[16]



(III)

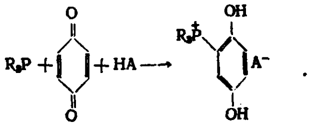
Tertiary phosphines readily react with quinones, forming products with P—O or P—C bonds,[17-20] whose structure is determined by the nature of the substituents in the quinone and the phosphine.

The addition of triphenylphosphine to *p*-benzoquinone leads to the phosphobetaine (IV):[4,17,18]

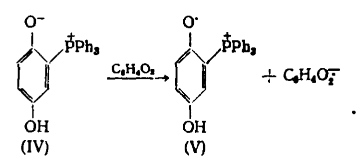


(IV)

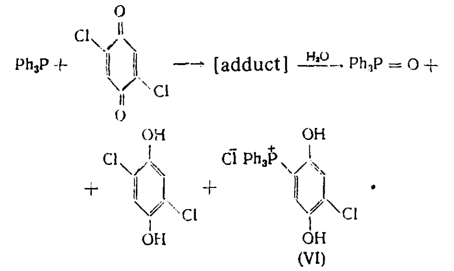
This reaction has been used to obtain a whole series of quaternary phosphonium salts, which are used to promote the interaction of vicinal epoxides with phenols and carboxylic acids or their anhydrides in order to obtain polymer films:[19]



The oxidation of the phosphobetaine (IV) can afford the paramagnetic radical-cation (V):[10,18]

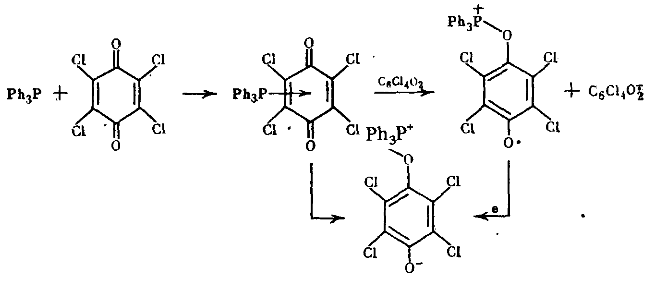


The interaction of triphenylphosphine with 2,5-dichloro-1,4-benzoquinone gives rise to an adduct, which is converted on treatment with water into diphenylphosphine oxide, 2,5-dichlorohydroquinone, and 2,5-dihydroxy-4-chlorophenyl(triphenyl)phosphonium chloride (VI):[20]

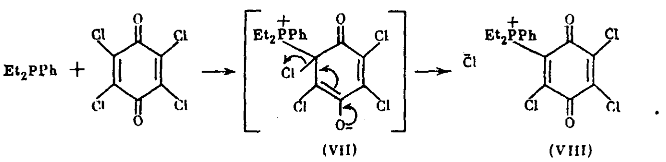


The EPR spectrum of the 2,5-dichloro-1,4-benzoquinone–triarylphosphine system, with a complex hyperfine structure of the signals, indicates the formation of phosphorus-containing paramagnetic species.[35]

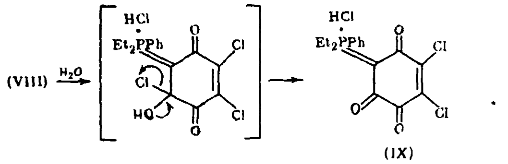
It has been demonstrated by UV and EPR spectroscopic methods that, in the reactions of triphenylphosphine with chloranil and also with bromoanil and iodanil, the paramagnetic products are formed mainly as a result of the oxidation by the quinone of phosphine–quinone charge-transfer complexes, but this is only one of the pathways leading to the final product:[17]



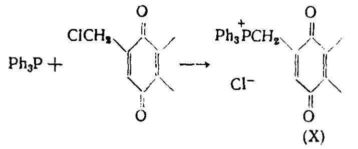
Diethylphenylphosphine reacts with chloranil to form the phosphorus-containing dipolar product (VIII), which is probably formed from the intermediate (VII):[21]



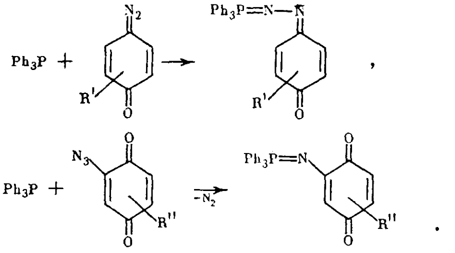
The chlorine atom in the *o*-position in the phosphabetaine (VIII) is readily substituted by a hydroxy-group from water, **which leads to a new type of stable phosphorus ylides (IX):**



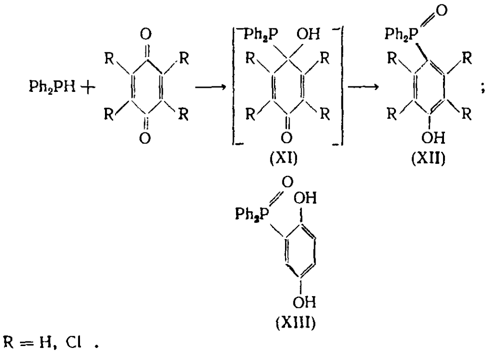
The interaction of phosphines with quinones having a chloromethyl substituent has been described. The main product is the phosphonium salt (X):[22]



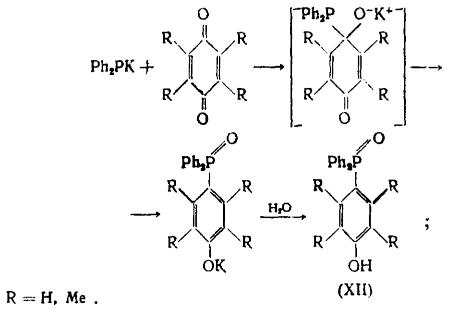
The adducts of phosphines with nitrogen-containing quinone derivatives also have a quinonoid structure:[4,23,24]



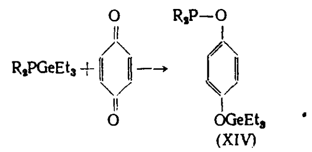
Secondary phosphines add to p-benzoquinones more vigorously than tertiary phosphines with formation of intermediates (XI) with a P–C bond, which are subsequently converted into the phosphine oxides (XII) [25] [however, according to other data,[26] the reaction product is compound (XIII)]:



The reaction apparently begins with nucleophilic attack by the phosphorus atom on the carbon of the carbonyl group.[25,27] It is accelerated with increase of the nucleophilicity of the phosphorus centre (for example, when hydrogen is replaced by an alkali metal[27]):

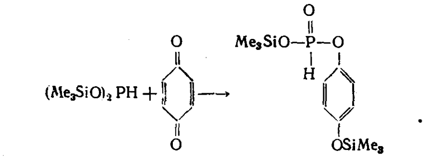


Dialkylgermylphosphine reacts with quinone via another mechanism. In this case the main product is *p*-triethylgermyloxyphenyl phosphinite (XIV)—a stable substance capable of being distilled, which was isolated from the reaction mixture in 50% yield:[28]

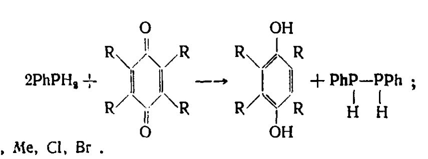


(XIV)

Silyl hypophosphites add to the 1,6-positions of p-benzoquinone without affecting the P–H bond:[29]

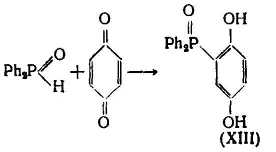


In contrast to secondary phosphines, primary phosphines do not add to quinones but reduce them to hydroquinones, being converted into diphosphines in this process:[30]



R = H, Me, Cl, Br .

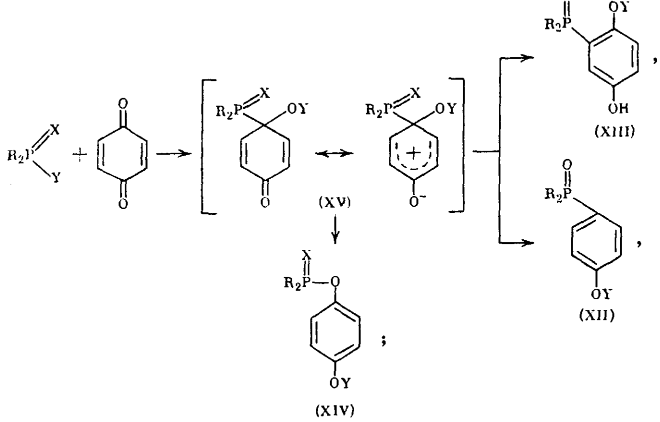
It is noteworthy that secondary phosphine oxides also react with quinones. The interaction of diphenylphosphinous acid with quinones leads to the C-phosphorylated adduct (XIII),[5,31] although, as will be shown below, almost all phosphorus-containing reagents having the general formula $R_2P{<}^{E}_{H}$ (R = AlkO, ArO, or Alk_2N: E = O, NR′, or S) react with quinones to form O-phosphorylation products:



(XIII)

It is believed[5] that this anomaly is caused by the involvement in the reaction of the tautomeric form of diphenylphosphinous acid with tricoordinate phosphorus.

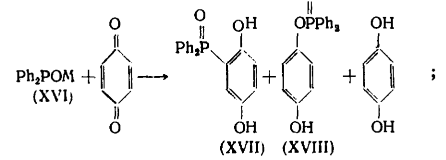
According to the views of other investigators, the intermediate (XV) is formed in this reaction and stabilised by being converted into the final C-phosphorylated hydroquinone (XIII):[7]



(XIII): R = Ar, X = O, Y = H: (XII): R = Ar, X = LEP (lone electron pair), Y = H, K; (XIV): R = Et, X = LEP, Y = GeR_3.

The characteristic features of the structure of the intermediate (XV) preclude the aromatisation process via the traditional deprotonation, since the ring carbon atom linked to the phosphorus group introduced contains no proton. Other pathways leading to the stabilisation of the cyclohexadienone, involving the migration of the phosphorus-containing group to the oxygen atom or a neighbouring carbon atom, are therefore followed.[7] Within the framework of the proposed scheme, one can also consider the mechanisms of the reactions of other organophosphorus compounds, namely diphenylphosphine, potassium diphenylphosphide,[25,27] and germylphosphine,[28] with p-quinones.

In contrast to diphenylphosphinous acid, its metal-substituted derivatives with p-benzoquinone to form both C- and O-phosphorylated products. For example, the phosphine oxide (XVII), the phosphinate (XVIII), and the hydroquinone in proportions of 1 : 1 : 1.5 and 1 : 0.5 : 1 have been isolated respectively in the reactions of lithium and magnesium salts of diphenylphosphinous acid (XVI) with p-benzoquinone:[32]

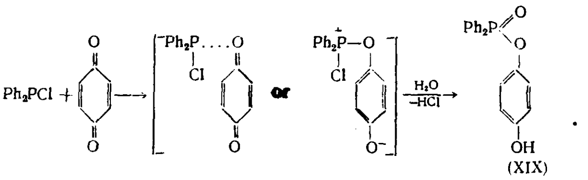


M = Li, MgCl.

The authors suggest that the phosphine oxide (XVII) is a result of the direct addition of the phosphinite (XVI) to a carbon atom of the quinonoid ring. The formation of two other products has been explained from the standpoint of the one-electron transfer mechanism.

In our view, the interaction can proceed via both the mechanism put forward by Koda et al.[32] and via the mechanism described above involving the initial addition of the phosphorus-containing reagent to a carbonyl group of the quinone and subsequent isomerisation of the intermediate (XV) to the O- and C-phosphorylation products.

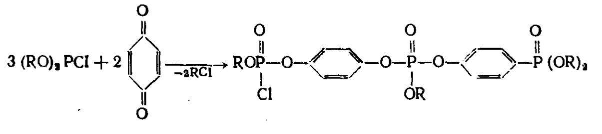
Chlorodiphenylphosphine reacts with quinone to form a 1 : 1 adduct to which the structure of a molecular or betaine-like complex has been attributed.[31] Treatment of the complex with water leads to the isolation of the O-phosphorylation product (XIX):



(XIX)

On the other hand, if the reaction is carried out in the presence of water, the C-phosphorylated hydroquinone (XIII) is formed. It is believed that chlorodiphenylphosphine hydrolyses to diphenylphosphinous acid, which is in fact the C-phosphorylating agent.[31]

Oligophosphates have been obtained in the reaction of dialkyl phosphorochloridites with 1,4-benzoquinone:[33]



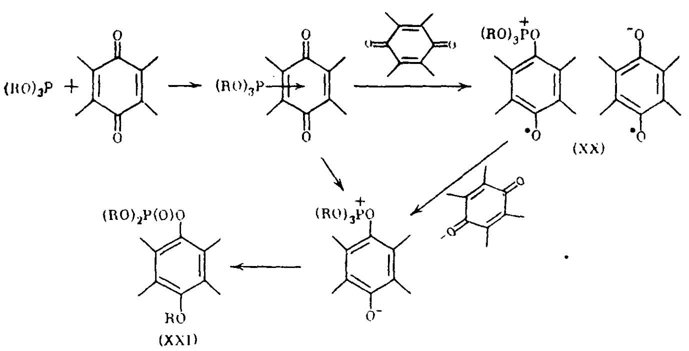
Thus the interaction of phosphines with quinones involves the intermediate formation of charge-transfer complexes and the subsequent structural reorganisation leads to the final reaction products. The pathway resulting in stabilisation depends significantly on the nature of the substituents in the reactants and in many cases can be interpreted in terms of the theory of hard and soft acids and bases.[21,34]

The formation of tertiary phosphine oxides (XII) and (XIII) is characteristic of secondary phosphines and metal phosphides.

Primary phosphines do not add to p-quinones and an oxidation-reduction process takes place instead.

2. Reactions of Phosphites with *p*-Quinones

All phosphite esters interact with p-quinone via the 1,6-addition mechanism.[2,3,21,35] This pathway predominates among other possible reaction pathways, since it leads to stable aromatic phosphates (XXI):



It has been suggested that the reaction mechanism involves the formation of the radical-ion pair (XX), but other pathways leading to the final products are also possible.[10,17]

Trimethyl phosphite adds to monosubstituted *p*-benzoquinones, affording mainly the O-phosphorylated adducts (XXII) and (XXIII) and sometimes the phosphonates (XXIV) (Table 1):[2]

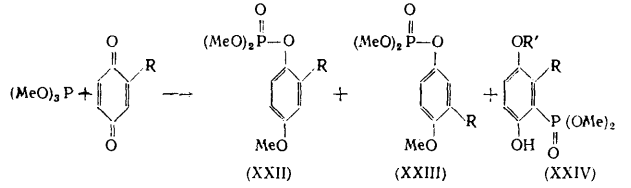
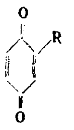


Table 1. The products of the reaction of trimethyl phosphite with *p*-benzoquinones.[2]

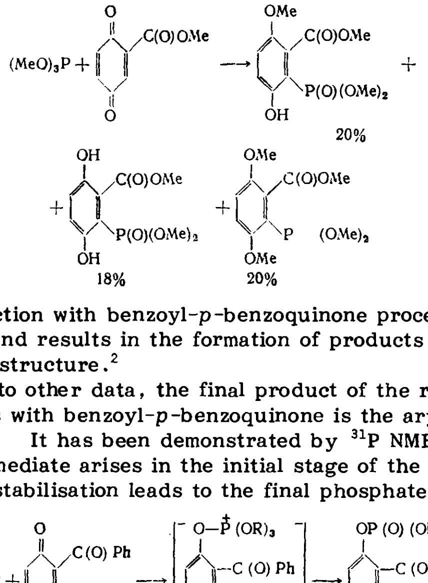


R	Yield of phosphate (XXII), %	Yield of phosphate (XXIII), %	Yield of phosphonate (XXIV), %*
OMe	79	2,5	—
Me	44	36	—
t-Bu	—	72	—
$SiMe_3$	—	67	—
CH_2OMe	17	50	—
Br	23	48	—
Cl	28	47	—
C(O)Ph	—	—	42
C(O)OMe	—	—	38

*The overall yield of the phosphonates (XXIV, R′ = H and Me).

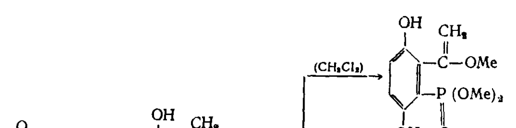
It has been established that the ratio of the phosphates (XXII) and (XXIII) is influenced by the nature of the substituent **R**. For example, the reaction with methoxy-p-benzoquinone produces mainly the 2-substituted aryl phosphate (XXII) and a small amount of the regioisomeric phosphate (XXIII). On passing to methyl-p-benzoquinone, the phosphorylation proceeds with a much lower degree of regioselectivity (Table 1). Nevertheless, t-butyl-*p*-benzoquinone and trimethylsilyl-p-benzoquinone react to form only the 3-substituted isomer (XXIII). Methoxymethyl-p-benzoquinone reacts with trimethyl phosphite to form the phosphates (XXII) and (XXIII) in proportions of 1 : 3, while in the reactions of bromo- and chloro-p-benzoquinones the products are in proportions of 1 : 2 (Table 1).

Only *C*-phosphorylated products have been detected in the reactions of trimethyl phosphite with quinones containing π-acceptor substituents. For example, phosphite reacts with methoxycarbonyl-*p*-benzoquinone to form phosphonates of type (XXIV):

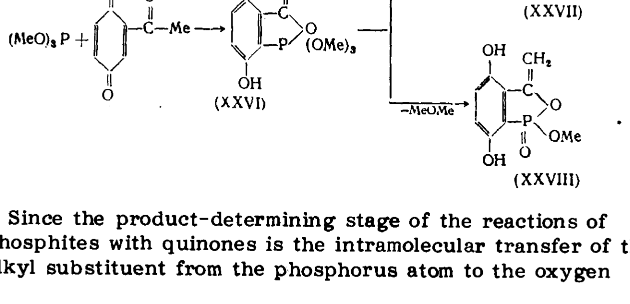


The interaction with benzoyl-*p*-benzoquinone proceeds analogously and results in the formation of products with the phosphonate structure.[2]

According to other data, the final product of the reactions of phosphites with benzoyl-*p*-benzoquinone is the aryl phosphate (XXV). It has been demonstrated by ^{31}P NMR that a dipolar intermediate arises in the initial stage of the reaction and that its stabilisation leads to the final phosphate (XXV):[36]

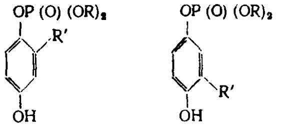


Acetylquinone reacts differently. It has been established that the phosphorane (XXVI) formed initially rearranges in CH_2Cl_2 to the methyl ester (XXVII). In other solvents, the phosphorane (XXVI) is converted into the cyclic phosphonate (XXVIII):[36]

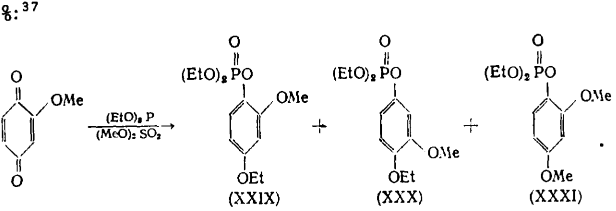


Since the product-determining stage of the reactions of phosphites with quinones is the intramolecular transfer of the alkyl substituent from the phosphorus atom to the oxygen atom in the *p*-position in the betaine intermediate, the addition of electrophiles to the reaction mixture can lead to the synthesis of non-traditional final compounds.

This type of result can be achieved when a source of protons is employed.[37] However, the method is not applicable to all quinones. Chlorotrimethylsilane is a more effective trapping agent. The reactions of quinones with the two-component phosphite/chlorotrimethylsilane system lead, after hydrolysis, to the formation of *p*-hydroxyaryl phosphates as the main product:[37]

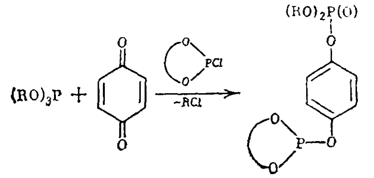


Dimethyl sulphate is yet another trapping agent. However, the reaction of triethyl phosphite with methoxy-*p*-benzoquinone in the presence of dimethyl sulphate affords the 4-ethoxyphosphates (XXIX) (49%) and (XXX) (12%). The yield of the expected 4-methoxyphosphate (XXXI) is only 5%:[37]

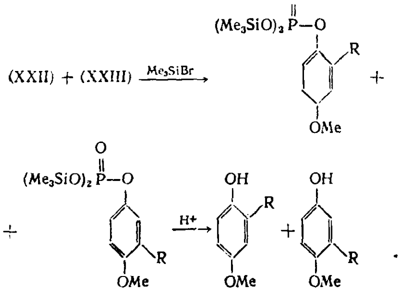


(XXIX) (XXX) (XXXI)

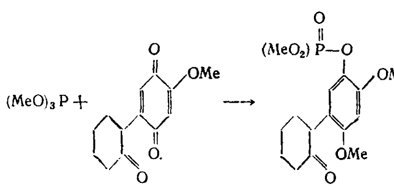
If cyclic phosphorochloridites are used as the trapping agents, then the products of the interaction of phosphites with *p*-benzoquinone are diphosphorylated hydroquinones. The compounds synthesised have many useful properties, in particular they impart fire resistance to materials:[38]



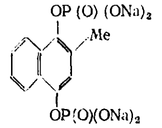
The hydrolysis of aryl dimethyl phosphates (XXII) and (XXIII) by refluxing in the NaOH/H₂O/ROH mixture or water in the presence of catalysts comprising a caesium fluoride[39] and the potassium fluoride cyclohexyl-18-crown ether system[40] gives rise to poor results, which may be a consequence of the tendency of electron-saturated dialkylphosphorylphenols to be oxidised, especially in basic media. The hydrolysis is more successful if the phosphates are subjected to preliminary dealkylation with bromotrimethylsilane and are converted into the corresponding silyl phosphates:[40]



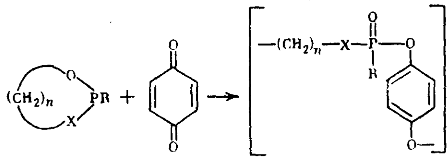
The interest in the reactions of phosphites with quinones has been aroused by the possibility of synthesising practically useful products, in particular biologically active preparations. The most convenient method of synthesis of 2-arylcyclohexanones, which are the basic compounds for the manufacture of the antibiotic "lysolipin I", is apparently based on this reaction:[2,41]



The tetrasodium salt of 2-methyl-1,4-naphthylene diphosphate, obtained from phosphite and 2-methyl-1,4-naphthoquinone, is one of the few radiosensitising agents for the radiotherapy of malignant tumours.[42] At a concentration of 4×10^{-6} M, this compound causes 50% suppression of mitosis in living tissues. It has been suggested that the action of this preparation consists in blocking the synthetic processes in cells associated with phosphorylation. It is noteworthy that the preparation itself has no therapeutic effect on malignant tumours.[42]



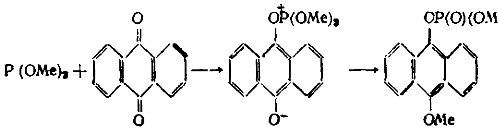
The synthesis of many industrial materials is based on the reactions of phosphites with quinones. For example, aromatic half-esters having the general formula $(OAr)_n$, used for the manufacture of moulded articles, adhesives, and fire extinguishing agents,[43] are formed by the reaction of substituted and unsubstituted quinones with compounds of tervalent phosphorus of the type $(RO)_2PR'$, while mixtures of cyclic phosphites and *p*-benzoquinone produce the polymers (XXXII), which have been used successfully as adhesives, plasticisers, and modifying agents reducing the combustibility of various chemical products:[44]



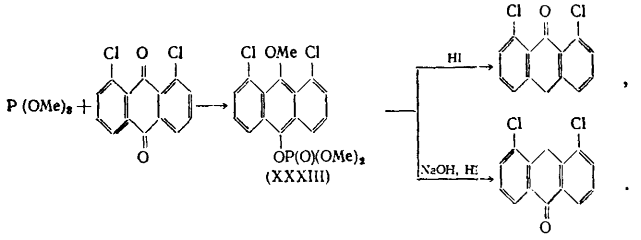
X = O, S, NR'.

(XXXII)

Under severe conditions, trimethyl phosphite is capable of adding to anthraquinone. The reaction mechanism includes two stages: the appearance of a dipolar intermediate and its isomerisation to the final 10-methoxy-9-dimethylphosphorylanthracene:[45]

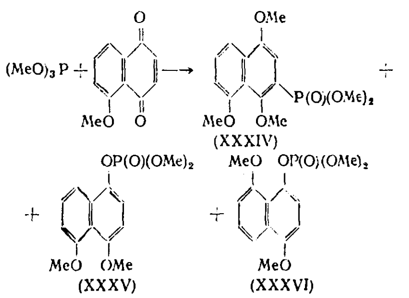


In the case of 1,8-dichloroanthraquinone, the relatively bulky phosphorus-containing residue enters the less hindered 10-position, while the methyl group enters the 9-position, forming the adduct (XXXIII):

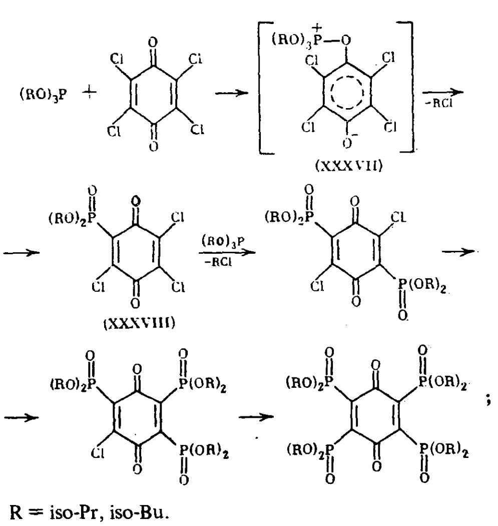


Selective hydrolysis of the methoxy- and phosphoryloxy-groups of the phosphate (XXXIII) and subsequent reduction of the hydrolysis products by hydriodic acid makes it possible to synthesise 1,8- and 4,5-dichloroanthrones which are otherwise difficult to obtain.[45]

The reactions of phosphites with naphthoquinones are less regioselective. Treatment of O-methyljuglone[5-methoxy-1,4-naphthoquinone] yielded all three possible isomeric products, the overall yield of the phosphates (XXXV) and (XXXVI) being lower than the yield of the phosphonate (XXXIV):[2]

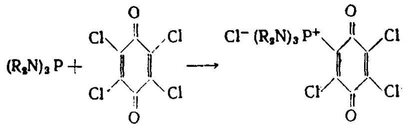


The reactions of phosphites having bulky alkyl substituents sometimes lead to unexpected results, in contrast to phosphites with unbranched substituents. Thus, instead of the usual addition to the quinone, the interactions of triisopropyl and triisobutyl phosphites with chloranil entail the substitution of the chlorine atoms in chloranil by phosphoryl groups. It has been suggested that the anomalous course of the reaction is caused by the steric hindrance of the dipolar intermediate (XXXVII), which is stabilised via the intramolecular Arbuzov reaction, affording the monophosphorylated quinone (XXXVIII). The latter reacts with the initial phosphite with successive substitution of the residual chlorine atoms in the quinone by phosphoryl groups:[46]

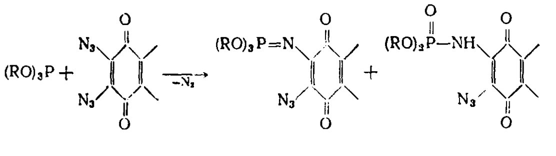


R = iso-Pr, iso-Bu.

Similar processes take place also in phosphorous triamides,[47] but in this system only one chlorine atom is substituted:

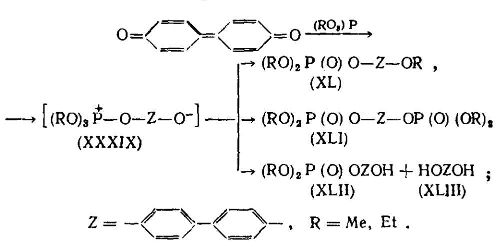


Trialkyl phosphites as well as phosphines react with azidoquinones. Although they are in the last place in the reactivity series of phosphoramidites (trialkylphosphines > triarylphosphines > trialkyl phosphites), nevertheless it is possible to isolate the products of their reactions with 2,3-diazidoquinone:[4,48]



Triaryl and trialkyl phosphorothioites do not react with azidoquinones.

The reactions of the full phosphite esters with diphenoquinone have been investigated in detail:[49]



4-Alkoxy-4′-biphenylyl dialkyl phosphate (XL), 4,4′-biphenylylene tetra-alkyl bisphosphate (XLI), dialkyl 4-hydroxy-4′-biphenylyl phosphate (XLII), 4,4′-dihydroxybiphenyl (XLIII), and the product of the self-polymerisation of diphenoquinone were isolated from the reaction mixture (Table 2).

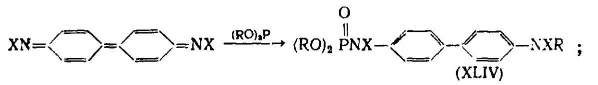
Table 2. Yields of the products of the reaction of $(RO)_3P$ with diphenoquinone[49]

R	Yields of products, %				
	(XL)	(XLI)	(XLII)	(XLIII)	Diphenoquinone polymer
Me	15	15	7	15	35
Et	17	15	5	*	50

*The yield was not accurately established.

The author suggests the following reaction mechanism. Initially there is nucleophilic addition of the phosphite to diphenoquinone with formation of the intermediate dipolar adduct (XXXIX), which subsequently rearranges to the phosphate (XL). According to the authors, the rearrangement proceeds via an intermolecular mechanism: the phenoxide oxygen of one molecule attacks the alkyl residue of another. When the object of attack by the phenoxide oxygen is the phosphorus atom, the process then terminates with formation of the bisphosphate (XLI). Owing to the inevitable presence of moisture, the adduct (XXXIX) hydrolyses and affords the phosphate (XLII) and dihydroxybiphenyl (XLIII). Together with the main reaction of the phosphite with diphenoquinone, another parallel reaction takes place—the polymerisation of diphenoquinone catalysed by the organophosphorus compound.

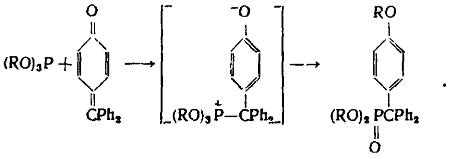
The products of the reactions of phosphites with diphenoquinoneimides are the phosphoramidates (XLIV), which have been isolated quantitatively:[49]



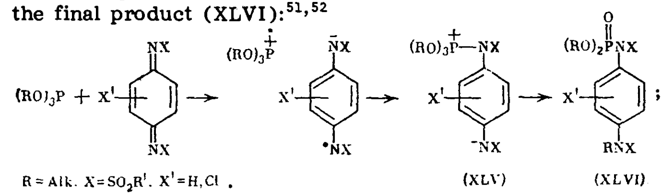
$X = SO_2Me$, SO_2Ph; $R = Me$, Et.

The reactivity of quinones in reactions with nucleophiles, including compounds of tricoordinate phosphorus, is determined both by the usual parameters (substituent, solvent, catalyst, etc.) and by specific parameters characteristic only of quinonoid systems. The latter include the oxidation-reduction properties of quinones. The redox potential of diphenoquinone (954 mV) is much higher than the potentials of "simple" quinones, for example chloranil (712 mV) or p-benzoquinone (696 mV).[4] This is in fact used to explain the significant differences between the reactions of phosphites with diphenoquinone.[49]

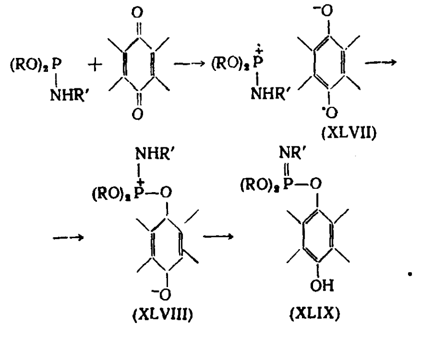
By virtue of the high electron-donating capacity of full phosphite esters, it is possible to achieve the reaction of quinonemethides with them. Fuchsone reacts with trialkyl phosphates on heating to form 1:1 adducts. As in most cases of the phosphorylation of *p*-quinones, in this instance the mechanism involves 1,6-addition to the conjugated bond system:[50]



The reaction with 1,4-benzoquinonebis-sulphonylimine begins with a one-electron transfer stage involving the formation of the phospite radical-cation and the quinonediimine radical-anion, whose interaction leads to the intermediate dipolar ion (XLV), which is transformed further into the final product (XLVI):[51,52]

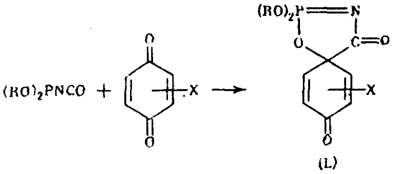


The amides of dialkylphosphorous acids readily interact with *p*-quinones, affording dialkyl *p*-hydroxyaryl *N*-organylphosphorimidates (XLIX):[53]



The signals of the chloroanil radical-anion and the phosphite radical-cation can be detected in the EPR spectra of the reaction mixture of *N*-acetylphosphoramidite and chloranil. A reaction mechanism has been proposed involving the initial formation of the radical-ion pair (XLVII), whose reaction via the stage involving the dipolar intermediate (XLVIII) leads to the final product (XLIX).[53]

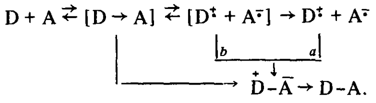
The interaction of *p*-benzoquinone with dialkyl phosphoroisocyanatidites is unusual: cycloaddition with participation of the carbonyl group in the quinone affords crystalline sparingly soluble oxazaphosphaspirocyclohexadienones (L):[54]



(L)

In the general case the interaction of compounds of tricoordinate phosphorus with *p*-quinones and their derivatives can be considered from the standpoint of one-electron transfer between the donor (D), i.e. the phosphorus(III) compound, and the acceptor (A), i.e. the *p*-quinone. This process is arbitrarily divided into three stages:[55] (1) the stage involving partial electron transfer (the formation of a charge-transfer complex); (2) the stage with total charge transfer (the formation of a radical pair in a solvent "cage"); (3) the stage involving the formation of fairly stable products (recombination or the emergence of the products from the "cage").

The following process mechanism can be put forward for the reactions of phosphorus(III) compounds with quinones:



$$D + A \rightleftarrows [D \to A] \rightleftarrows [D^{\dot{+}} + A^{\dot{-}}] \to D^{\dot{+}} + A^{\dot{-}}$$
$$\overset{+}{D}-\overset{-}{A} \to D-A.$$

Complexes $[D \to A]$ with partial electron transfer are formed initially and are followed by complexes $[D^{\dot{+}} + A^{\dot{-}}]$ with complete electron transfer. The radical-ion pair then emerges from the solvent "cage" and the free paramagnetic radical-ions $D^{\dot{+}}$ and $A^{\dot{-}}$ appear and in many cases can be detected by chemically induced dynamic nuclear polarisation (CIDNP) and electron paramagnetic resonance (EPR) methods. The recombination of the radical species via pathway *a* or *b* leads to the dipolar structures $\overset{+}{D}-\overset{-}{A}$, which in the case of phosphines are the final reaction products. The betaines $\overset{+}{D}-\overset{-}{A}$ can also be stabilised directly starting with the complex $[D \to A]$, by-passing the one-electron transfer stage.[10] The majority of the processes occurring in the phosphite (phosphine)—*p*-quinone system fit within the framework of the proposed mechanism.

3. The Reactions of Tricoordinate Phosphorus with o-Quinones

The polarographic method has been applied to the study of electron affinities of various quinones (Table 3).

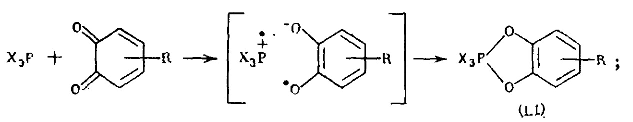
When a number of *o*- and *p*-quinones were reduced, two one-electron reduction stages with fairly different half-wave potentials were observed.

The data in Table 3 permit the following conclusions: firstly, *o*- and *p*-quinones have similar electron affinities and one-electron transfer with the intermediate formation of radical-ions is therefore also possible for the reactions of *o*-quinones; secondly, the smaller difference between the first and second half-wave potentials ΔE for o-quinones compared with p-quinones shows that the transition from the one-electron mechanism to the two-electron mechanism is easier for o-quinones than for p-quinones.[56]

Table 3. Polarographic characteristics of the reduction of quinones.[56]

Quinone	$E'_{1/2}$, V	$E''_{1/2}$, V	$\Delta E = E''_{1/2} - E'_{1/2}$
Chloranil	−0.25	−1.17	−0.92
p-Benzoquinone	−0.56	−1.53	−0.97
Naphthoquinone	−0.81	−1.70	−0.89
Tetrabromo-*o*-benzoquinone	0.15	−0.57	−0.72
Tetrachloro-*o*-benzoquinone	−0.25	−0.61	−0.36
9,10-Phenanthrenequinone	−0.60	−1.23	−0.63
4,5-Dimethoxy-1,2-benzoquinone	−0.70	−1.20	−0.50

It has been established that both phosphines and phosphites react with *o*-quinones, affording adducts with the phosphorane structure (LI):[3,13,57]



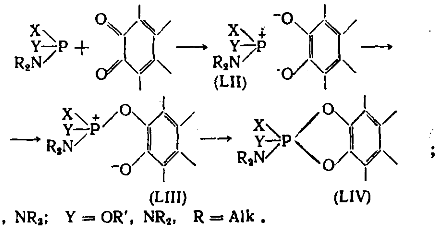
(LI)

X = Alk, Ar, AlkO, ArO, Cl .

A process mechanism incorporating a one-electron transfer stage, analogous to the mechanism of the reactions of phosphorus(III) compounds with *p*-quinones examined previously, has been proposed on the basis of kinetic and spectroscopic data.[58]

Phosphorus trichloride interacts with tetrachloro-*o*-benzoquinone, 9,10-phenanthrenequinone, 4,6-di(t-butyl)-1,2-benzoquinone, and 1,2-naphthoquinone, forming trichloro-1,2-phenylenephosphoranes (LI). A characteristic doublet signal, due to the interaction of the unpaired electron with the phosphorus nucleus, can be observed in the EPR spectra of the reaction mixtures, which indicates the possibility of the appearance of phosphorus-containing radical-ion species in the course of the reaction.[59]

EPR study of the interaction of phosphoramidites with tetrachloro-o-benzoquinone showed that the o-chloranil radical-anion and the phosphoramidite radical-cation (LII) exist for a time in the reaction mixture. The authors suggested that involvement of these species in the formation of the dipolar intermediate (LIII), which is converted into the final phosphorane (LIV):[56,57]

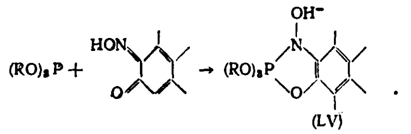


(LII) (LIII) (LIV)

X = OR', NR₂; Y = OR', NR₂, R = Alk .

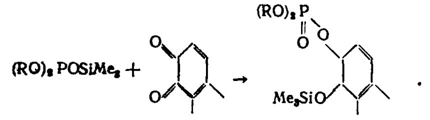
Phosphoramidites interact analogously with tetrabromo-*o*-benzoquinone. The one-electron transfer mechanism does not operate in all the reactions of 9,10-phenanthrenequinone, which has a smaller electron affinity (see Table 3), with phosphoramidites. On passing to 4,5-dimethoxy-1,2-benzoquinone, which is a still weaker acceptor, the formation of paramagnetic species is never detected. This confirms the conclusion that the replacement of the one-electron mechanism by the two-electron mechanism is more probable for *o*-quinones than for p-quinones.

The overall mode of reaction of phosphites with *o*-quinones, leading to the formation of phosphorane adducts, persists also for *o*-quinone monoximes. On reaction with phenanthrenequinone monoxime, trialkyl phosphites give rise to cyclic nitrogen-containing phosphoranes (LV), from which the initial quinone oxime can be regenerated:[60]



(LV)

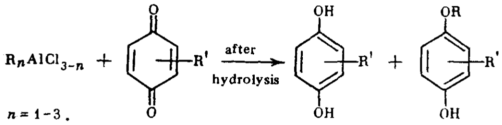
Silicon-containing phosphites react with *o*-quinones in the same way as with *p*-quinones, producing *o*-siloxyaryl phosphates:[61-63]



The absence from the given process of products with a pentacoordinate phosphorus atom is probably associated with their instability and ready isomerisation to aryl phosphates as a consequence of the high lability of the trimethylsilyl group.[14]

It is of interest to compare the reactivities of tricoordinate phosphorus compounds and other organoelemental nucleophiles in reactions with quinones. It has been established that the incompletely substituted alkyl(aryl)chloro(silanes) react on heating with *p*-benzoquinone in the presence of platinum catalysts, affording silyl ethers of hydroquinone.[64]

Hydroquinones and their monoalkyl ethers have been synthesised by the reaction of organoaluminium compounds with *p*-quinones and subsequent hydrolysis of the products:

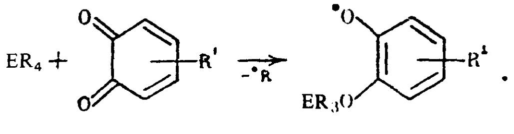


Paramagnetic intermediates—aluminium salts of semiquinone—were detected in the reaction of triethylaluminium and aluminium chloride with *p*-benzoquinone.[65]

2-Alkyl-3-chloro-1,4-naphthoquinones can be obtained from a mixture of trialkylaluminium with 2,3-dichloro-1,4-naphthoquinone. Similar naphthoquinones are formed in the reaction with participation of alkylzinc chlorides and tetra-alkylstannanes.[66] When gallium trichloride interacts with *p*-benzoquinone, 2:1 complexes are produced. The dipole moments for the formations of these compounds were determined by dielectric constant measurements.[67]

Thus organotin, organozinc, organoaluminium, and organosilicon, as well as organoantimony and organoarsenic compounds[68,69] do not add to *p*-quinones, in contrast to phosphorus(III) reagents, but convert them into alkylquinones, alkylhydroquinones, and hydroquinone ethers, the reactions requiring heating and the use of catalysts. However, despite the significant difference between the types of interaction of organophosphorus and other organoelemental compounds with *p*-quinones, the majority of the reactions proceed via a stage involving the formation of radical-ion species.[65,68,69]

The reactions of various metal halides with *o*-quinones have been studied in detail. The investigation of the EPR spectra of complexes of 1,2-naphthoquinone and 9,10-phenenthrenequinone with aluminium, gallium, and indium halides led to the conclusion that the compounds MX_3 exhibit electron-donating properties in relation to *o*-quinones. Electron transfer from the metal halides to the *o*-quinone molecule with formation of a paramagnetic chelate complex has been suggested.[70] Paramagnetic complexes were also obtained in reactions of *o*-quinones with organometallic compounds ER_4 (E = Sn, Si, or Ti; R = alkyl or halogen):

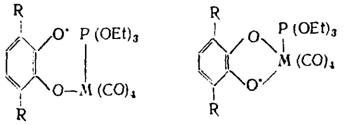


The reaction of tin tetrachloride with 3,6-di(t-butyl)-1,2-benzoquinone resulted in the formation of the *o*-benzosemiquinone complex, which a tetragonal pyramidal structure assigned on the basis of spectroscopic data.[71]

Evidently in their reactions with *o*-quinones organoelemental compounds having an unshared electron pair behave as electron-donating agents and, depending on the nature of the central atom and its environment, form cyclic or acyclic adducts.

In conclusion of this Section, devoted to a survey of studies on the reactions of phorphorus(III) compounds with quinones, the *o*-semiquinonoid complexes of metals with phosphite ligands must be considered.

The photolysis of metal decacarbonyls produces the radicals $M(CO)_5$ (M = Mn or Re),[72] whose interaction with *o*-quinones and triethyl phosphite leads to the appearance of the primary radical (LVI), which is converted further into the secondary radical (LVII):[73]



(LVI) (LVII)

M = Mn, Re; R = t-Bu.

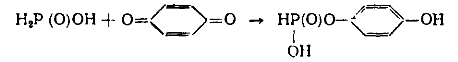
Kinetic measurements have shown that the rate of conversion (k = 0.0013 s^{-1}) of the radical (LVI) into the radical (LVII) is appreciably lower than the rate of conversion (k = 0.017 s^{-1}) of the analogous non-phosphorus radicals.[73] The large difference between the rate constants for the destruction of the primary radicals as a function of the presence of the phosphite ligand has been attributed to the influence of the electron-accepting properties of triethyl phosphite on the rate-limiting stage of the process.[74] It also follows from the EPR spectra that the substitution of a CO group by a triethyl phosphite molecule in the radical (LVI) and (LVII) shifts the electron density from the *o*-quinonoid ligand to the phosphorus atom.

A similar conclusion follows from the analysis of the electronic absorption spectra of complexes of types (LVI) and (LVII). It has been suggested that the shift of electron density as a result of exchange interactions between the phosphorus and oxygen atoms proceeds via the *d* orbitals of the metal atom by virtue of the coplanarity of these atoms.[73,75]

III. COMPOUNDS OF TETRACOORDINATE AND PENTACOORDINATE PHOSPHORUS

1. Reactions of Dialkyl Phosphites with Quinones

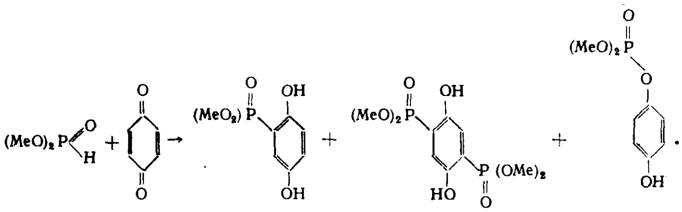
Almost all hydrophosphoryl compounds give rise to *O*-phosphorylation products in their reactions with quinones.[76-84,109] Hydrophosphites are no exception. The reaction of *p*-benzoquinone with 50% hypophosphorous acid results in the formation of reduction products—quinhydrone and hydroquinone, but, when this reaction is carried out in an anhydrous medium or in the presence of a small amount of water, an adduct, namely mono-*p*-hydroxylphenyl phosphite (yield up to 46%), is formed together with the benzoquinone reduction products:[76,77]



$$H_2P(O)OH + O{=}C_6H_4{=}O \rightarrow HP(O)(OH)O{-}C_6H_4{-}OH\ .$$

It has been established that dialkyl phosphites add to various *o*- and *p*-quinones, forming dialkyl hydroxyaryl phosphates.[78-84] The reaction is accelerated in the presence of bases, but can proceed also via a homolytic pathway.[7]

An exception to this general rule is the interaction of dimethyl phosphite with *p*-benzoquinone, which leads to the formation of the *C*-phosphorylated product (LVIII) and the *CC*-diphosphorylated product (LIX). An adduct having the phosphate structure has also been detected in the reaction mixture:[85]



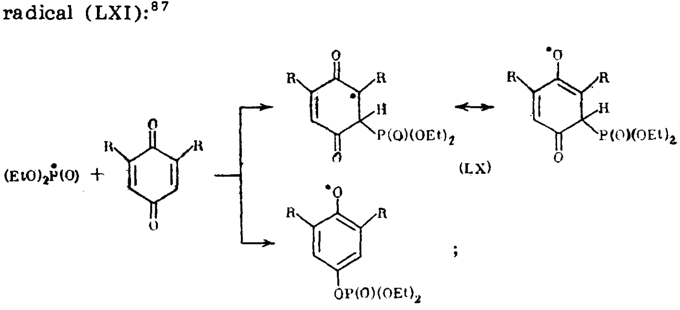
(LVIII) (LIX)

The photolysis of the corresponding hydrophosphoryl compounds in the presence of di(t-butyl) peroxide leads to the formation of phosphoryl radicals:[86]

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO^{\cdot}\ ,$$

$$(RO)_2P(O)H + {}^{\cdot}OCMe_3 \xrightarrow[-Me_3COH]{} (RO)_2\dot{P}(O)\ .$$

These radicals add to 2,6-di(t-butyl)-1,4-benzoquinone, affording the phosphonate radical (LX) and the phosphate radical (LXI):[87]



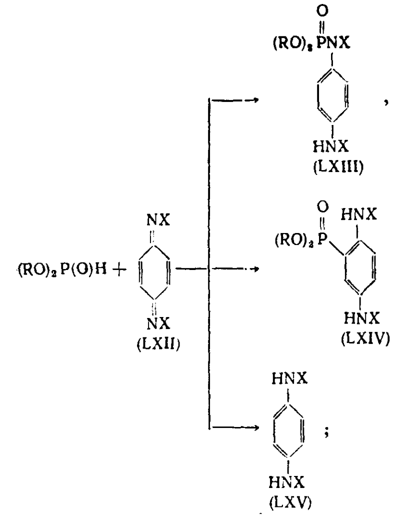
(LX)

R = t-Bu. (LXI)

Species with an analogous structure are formed in the reactions of phosphonyl radicals with quinonemethides and 3,3,5,5-tetra(t-butyl)diphenoquinone.[87]

The synthesis of phenoxy-radicals of types (LX) and (LXI) by easy methods is a problem of current importance whose solution would lead to prospects for the synthesis of a wide variety of phosphorus-containing aromatic compounds.

Dialkyl phosphites react with p-benzoquinonebisbenzenesulphonylimine (LXII), forming a mixture consisting of the phosphoramidate (LXIII), the phosphonate (LXIV), and the bisamide (LXV):



R=Alk, X=SO_2Ph .

The yield of the compounds depends on the nature of the phosphite reagent, the molar ratio of the reactants, and the reaction conditions (Table 4).[88]

Table 4. The reaction of $(RO)_2P(O)H$* with p-benzoquinonebisbenzenesulphonylimine (LXII).[88]

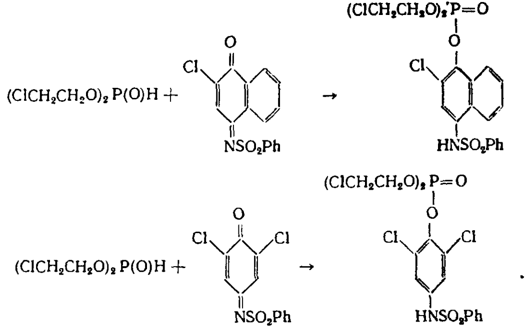
R	Solvent	t, °C	Duration, h	Yields of products, %		
				(LXIII)	(LXIV)	(LXV)
Me	—	25	48	25	40	30
Me	—	110	2	10	20	65
Me	—	140	2	10	15	70
Me **	—	100	3	—	—	>95
Me	benzene	25	72	20	45	30
Me	benzene	refluxing	10	20	30	45
Et	—	25	48	35	45	15
Et	—	110	2	20	25	50
Et	—	140	2	15	20	60
Et **	—	100	3	—	—	>95
Et **	benzene	refluxing	6	—	—	>95
изо-Pr	benzene	refluxing	4	—	>95	—

*The ratio $(RO)_2P(O)H$: (LXII) = 15 : 1.
**$(RO)_2P(O)H$ with a low purity.

All three products are obtained from dimethyl and diethyl phosphites, while diisopropyl phosphite gives rise to only the phosphonate (LXIV) (see Table 4). It has been noted that the quinoneimine (LXII) reacts with dialkyl phosphites only in the presence of a fifteenfold excess of the phosphite. If the amount of phosphite is less, then the reaction does not occur whatever the conditions. This is true only for freshly distilled dialkyl phosphites. When reagents with a low degree of purity are used, hydrolysis results in the formation of phosphorous acid, which has powerful reducing properties. Under these conditions, the main reaction product is the bisamide (LXV) (Table 4).

An increase of temperature and reaction time decreases the yields of the phosphorus compounds and increases the yield of the bisamide (LXV). The presence or absence of the solvent in the reaction mixture has almost no effect on the ratio of the reaction products.[88]

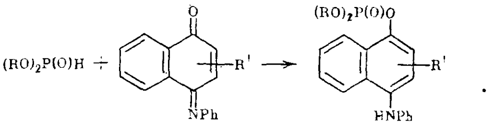
In order to obtain practically useful compounds, di(chloroalkyl) phosphites were introduced into the reaction with quinoneimines:



The resulting 2-chloro- or 2,6-dichloro-arene-4-sulphonamidoaryl di(chloroalkyl) phosphates have been recommended as additives to oils and fuels.

In contrast to the reactions of unsubstituted dialkyl phosphites, this process proceeds more vigorously, requiring a lower temperature to initiate the reaction.[89]

p-Quinone anils combine with dialkyl phosphites to form O-phosphorylated adducts:[84]

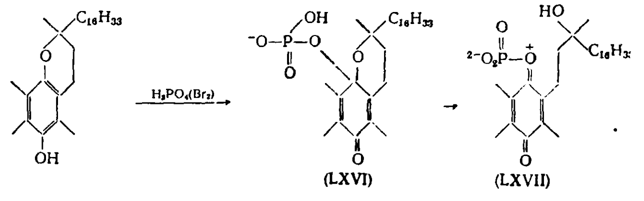


2. Reactions of Phosphates with Quinones

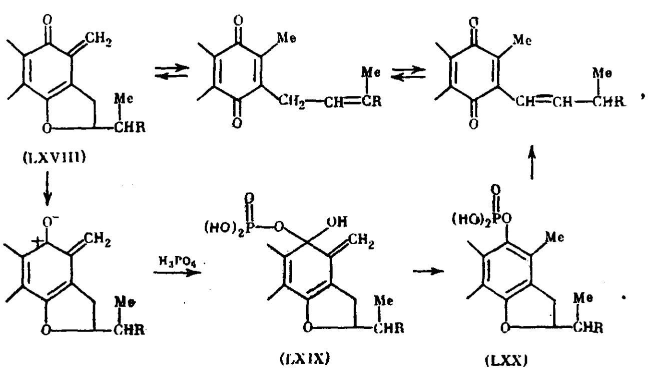
Many natural products, isolated from higher and lower plants and animals, belong to the class of quinones. They include dyes, growth regulators, antibiotics, and catalysts of respiratory processes. For example, juglone, detected in the roots and leaves of the walnut tree, exhibits a pronounced allelopathic activity, lawsone, the yellow pigment of henna leaves, is known as a fungicide, plumbagin, identified in the roots, stems, and leaves of certain tropical plants, is a mirobicide, and quinones of the vitamin K series, contained in micro-organisms and plants, are catalysts of the biosynthesis of certain proteins.[90]

The interest of chemists in the reactions of such natural products with various reagents, including organophosphorus reagents, is understandable, because such investigations are closely related to the synthesis of promising biologically active preparations.

It has been found that the product of the reaction of the natural terpene tocopherol with phosphoric acid tocopheroxide (LXVI), whose acetal phosphate group is capable of phosphorylating adenosine diphosphoric acid with formation of its triphosphoric acid analogue—the energy source in cell processes. The active principle is in this instance the quinonoid system (LXVII), which acts as a phosphorylating agent:[91]

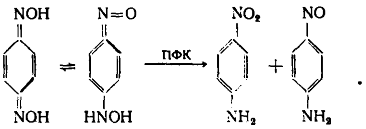


Phosphoric acid also adds to one of the active forms of vitamin K_1 (LXVIII) with formation of the phosphate (LXIX), which is subsequently reduced by flavin-nucleotide to the phosphate (LXX). On treatment with adenosine diphosphate and cytochrome, the latter gives rise to the initial quinone and adenosine triphosphoric acid:[92]

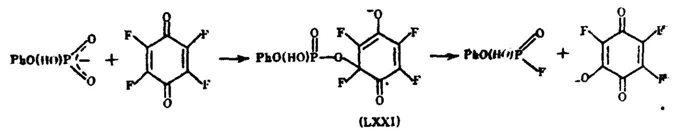


(LXVIII) (LXIX) (LXX)

It has been established that in the presence of an excess of polyphosphoric acid (PPA), quinone dioxime disproportionates with formation of p-nitroaniline and p-nitrosoaniline, which can be isolated respectively from diluted and neutralised solutions:[93]



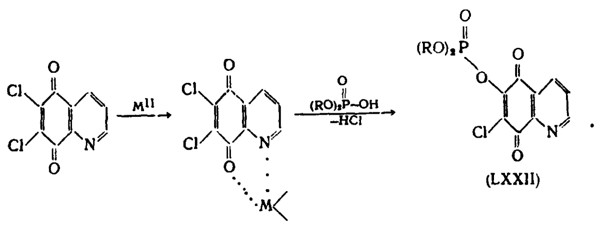
The anion of the phenyl ester of phosphoric acid, which is an active nucleophile, interacts with fluoranil. The fragmentation of the intermediate (LXXI) formed initially leads to the final reaction products:[94]



(LXXI)

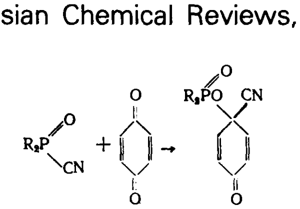
This reaction can be used as a method of synthesis of phosphorofluoridic acids.

Dialkylphosphoric acids do not interact with 6,7-dichloroquinoline-5,8-quinone, but in the presence of transition metal ions the reaction does occur. The products of the catalytic process are substituted quinolinequinones (LXXII). The activating effect of the metal ion has been explained by the increase of the deficiency of electron density at the C(6) atom, which promotes the substitution of the chloro-group in this position (as the chloride anion) by the phosphoryl group:[95]

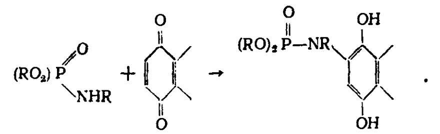


(LXXII)

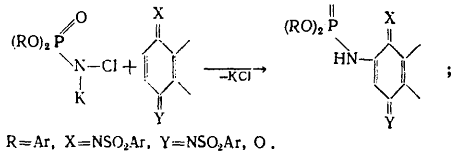
A rare variant of the nucleophilic addition to a C=O bond of the quinone occurs in the reactions of phosphinic acid cyanides with p-benzoquinone:[96]



Phosphoramidates having the N–H bond interact with quinones, forming phosphorylated 1,4-adducts:[47]



It has been established that quinoneimines can be aminated by N-chlorophosphoramidates:[97]

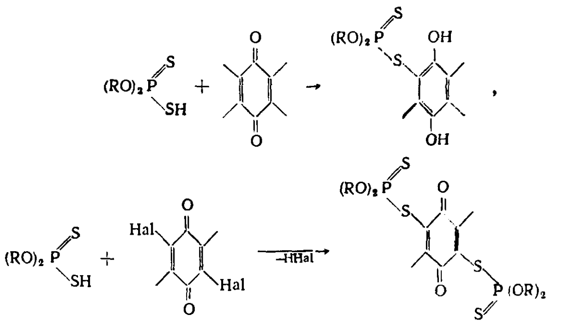


R=Ar, X=NSO_2Ar, Y=NSO_2Ar, O.

Among compounds of tetracoordinate phosphorus, sulphur-containing phosphates have been studied in greatest detail in their reactions with quinones because their preparative and kinetic investigation is easy.

The interaction of phosphorodithioates with quinones proceeds readily and fairly selectively in the absence of catalysts. The reaction products can be isolated from the reaction mixture quantitatively, do not require special purification, and their identification presents no difficulties. Phosphorodithioates and quinones are uncommonly suitable reactants for kinetic and spectroscopic studies. The advantages enumerated above as well as the ready availability and stability of the initial compounds have made the reactions of phosphorodithioic acids with quinones irreplaceable as objects of comprehensive and profound study.

Phosphorodithioic acids enter into addition[98] or substitution[99] reactions with quinones and their halogeno-derivatives:



The products have found applications in veterinary science and the pharmaceutical industry and are used as antioxidants and insecticides. As representatives of the class of phosphorodithioates, they are characterised by a broad spectrum of insectoacaricidal activity, rapidity of action, small consumption of the preparation per unit area treated, and the absence of toxic residues. They are most effective in the fight against insect species resistant to other organophosphorus insectoacaricides.[100]

It has been found that the silyl esters of phosphorodithioic acid are also capable of adding to p-quinones with formation of 1,4-addition products.[101]

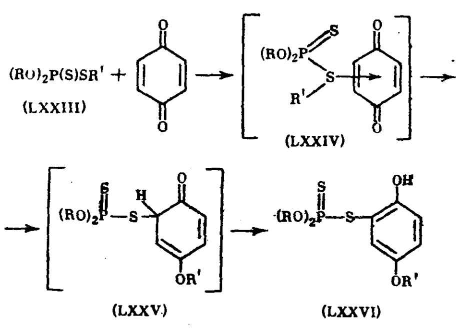
Spectrophotometric study of the reaction involving the addition of phosphorodithioic acids and silyl phosphorodithioates to *p*-benzoquinone showed that the rate of reaction is described by a second-order equation, of first order with respect to each reactant. Silyl phosphorodithioates are less reactive in heptane than the corresponding acids and the sensitivity of the reaction to the influence of substituents at the phosphorus atom is low. Whereas a tendency for the reaction to be accelerated with increase of the acidity of individual groups of dithio-derivatives of phosphorus (phosphates, phosphonates, and phosphinates) has been traced, overall there is no such trend. This may be a consequence of the important role of not only the acid but also the nucleophilic properties of phosphorodithioates in the addition reaction.[103]

An appreciable increase of the rate of reaction is observed in basic solvents. In the correlation equations taking into account the influence of the polarity, polarisability, and specific properties of the medium[102] on the rate of reaction of *OO*-diethylphosphorodithioic acid and its *S*-trimethylsilyl ester with *p*-benzoquinone, only the contribution of the nucleophilic solvation of the solvent is statistically significant.[103]

On passing to media with pronounced nucleophilic properties, the reactivity of silyl phosphorodithioates becomes comparable in terms of rate of reaction to that of phosphorodithioic acids.

In order to elucidate the cause of such relations, the deuterium kinetic isotope effects (KIE) have been investigated for phosphorodithioic acids and *p*-benzoquinone in various solvents. In all cases the "reverse" KIE is observed for the dithio-acids, which indicates an appreciable strengthening of the binding of the hydrogen atom in the transition state of the proton transfer stage from the phosphorus-containing reactant (LXXIIIa) to *p*-benzoquinone and may be a consequence of the fact that the activated complex has a structure resembling that of the intermediate (LXXV).[104]

When deuteriated *p*-benzoquinone was used, the KIE for the reaction with phosphorodithioates (LXXIIIa, b) in heptane and benzene proved to be unity, i.e. the migration of the ring proton takes place after the rate-limiting stage of the reaction. In basic media (dioxan, acetonitrile), where the KIE exceeds unity, the conversion of the intermediate (LXXV) into the product (LXXVI) becomes rate-determining. An analogous pattern of changes in the KIE for *p*-benzoquinone has been observed also in the reaction with *OO*-diethyl *S*-trimethylsilyl phosphorodithioate.

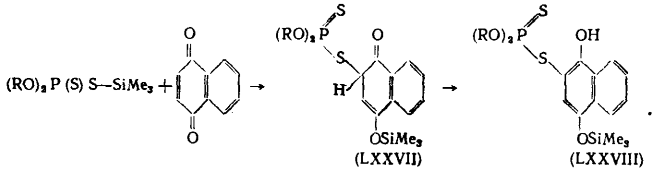


(a) R'= H (D):(b)R' = Si .

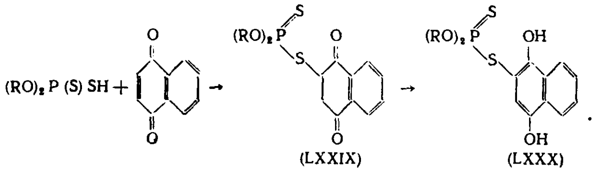
The set of data examined suggests that the addition of phosphorodithioates to *p*-benzoquinone proceeds in accordance with the scheme presented above. The fact that the same mechanism operates in the interaction of phosphorodithioic acids (LXXIIIa) and their *S*-trimethylsilyl esters (LXXIIIb) with quinone has been confirmed by the correlation between lg *k* for both processes in the media employed.[103]

In view of the high electron-accepting capacity of *p*-benzoquinone [105] and the appreciable nucleophilicity of the sulphur in phosphorodithioates,[106] the initial formation of a complex of the *n*–π type (LXXIV) may be postulated. Its concentration and stability are evidently low, since it is not detected spectroscopically. This factor does not in its turn rule out the possibility of the reversal of the initial step of the interaction under certain experimental conditions. Next, the complex is converted endothermically into the intermediate (LXXV) and in weakly basic media this process is rate-determining, so the silyl phosphorodithioates are more reactive than phosphorus acids. The presence of the complex formation stage and the appearance of a late rate-limiting transition state explain the low sensitivity of the rate of reaction to the influence of substituents at the phosphorus atom and to the dielectric properties of the medium.[107] In markedly nucleophilic solvents, the transfer of the ring proton to the carbonyl group of the intermediate, (LXXV) → (LXXVI), becomes rate-determining and the reactivity of silyl phosphorodithioates is comparable, in terms of the rate of reaction, to that of phorphorus acids.

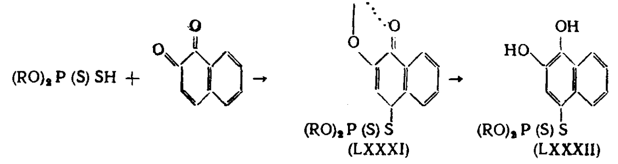
The interaction of phosphorodithioic acids and silyl phosphorodithioates with 1,4-naphthoquinone proceeds in accordance with a mechanism formally analogous to that in the reaction with *p*-benzoquinone. In the case of silyl phosphorodithioates, the 1,4-adduct (LXXVII) is formed as an intermediate, as in the reaction with *p*-benzoquinone:



However, it follows from the analysis of the time variation of the IR spectra of a mixture of solutions of 1,4-naphthoquinone and the dithio-acid that a product (LXXIX) of the addition to a C=C bond of the quinone is formed initially and is then gradually converted into dihydroxyphosphorothioylthionaphthalene (LXXX):[108]



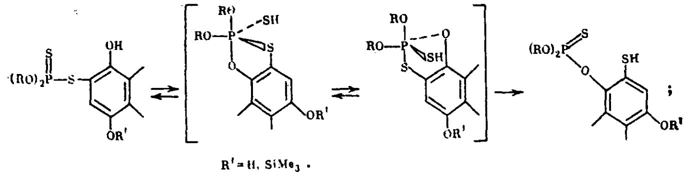
The reaction of phosphorodithioic acids with 1,2-naphthoquinone is unusual. The intermediate (LXXXI), detected by IR spectroscopy, isomerises over a period of time to the final adduct (LXXXII):



The stability of the enolic form of the intermediate (LXXXI) is apparently due to the energy gain by the system as a result of the formation of a stable intramolecular hydrogen-bonded complex.[108]

Thus the mechanism of the reactions of phosphorodithioic acids with quinones depends on the structure of the unsaturated reactant and involves the initial addition either to a C=C double bond or to the C=C – C=O conjugated system; silyl phosphorodithioates form initially 1,4-adducts in all cases.

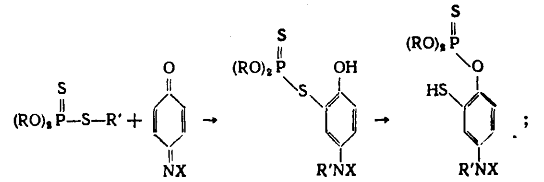
The final products of the reactions of phosphorodithioates with the *p*-quinones (LXXVI), (LXXVIII), and (LXXX) are capable of isomerising on heating to the corresponding phosphoromonothioates.[103,107] The mechanism of the rearrangement involves the intermediate formation of mercaptophosphoranes:



R' = H, SiMe$_3$.

Kinetic study of the isomerisation,[103,107] which takes place via a unimolecular mechanism, showed that the influence of the nature of the substituents at the phosphorus atom is determined by a set of electronic and steric factors and obeys the rules of the "hydroxyphosphorane concept".[110]

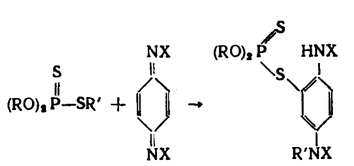
The interaction of phosphorodithioates with *N*-benzenesulphonyl-1,4-quinoneimine affords 5-(*N*-benzenesulphonamido)-2-hydroxyphenyl phosphorodithioates (LXXXIII), which isomerise to the corresponding phosphoromonothioates (LXXXIV):



(LXXXIII) (LXXXIV)

R'=H, SiMe$_3$; X=SO$_2$C$_6$H$_5$.

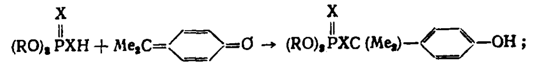
On passing to 1,4-quinonediimines, the reaction stops at the adduct (LXXXV) formation stage:[101]



(LXXXV)

R'=H, SiMe$_3$; X=SO$_2$Ph .

Phosphates and phosphorodithioates also add to quinonemethides, the reaction resulting in the formation of 1,6-adducts:[111]



$$(RO)_2\overset{X}{\overset{\|}{P}}XH + Me_2C{=}C_6H_4{=}O \rightarrow (RO)_2\overset{X}{\overset{\|}{P}}XC(Me_2){-}C_6H_4{-}OH\,;$$

X=O, S .

It is noteworthy that not only phosphorodithioic acids but also other organic compounds with a mobile hydrogen atom, for example, alcohols, amines,[4,12,112,113] mercaptans,[114,115] and carboxylic,[116] sulphinic, and sulphonic acids and their derivatives[117,118] react readily with quinones. The reductive aromatisation of the quinonoid systems is the driving force of these processes.

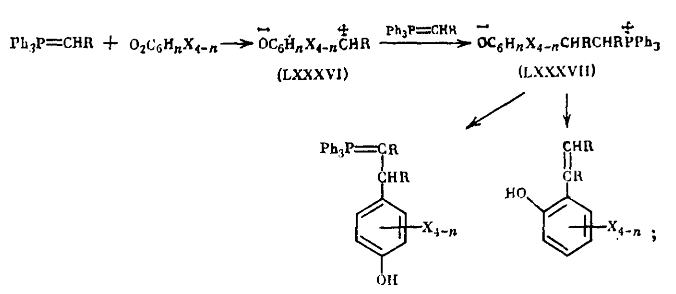
Comparison of the reactivities of phosphites and phosphates has shown that, apart from aromatisation, the formation of the extremely stable P=O bond promotes the reactions with quinones. This factor gives rise to process energetics such that in the case of phosphites addition in the 1,6-positions in the *p*-quinone takes place.

On the whole, *Ad* processes of this kind are encountered extremely rarely in the chemistry of *p*-quinones and occur only in certain cases.[78,119,120]

The structure of phosphates rules out the possibility of the formation of the phosphoryl group, so that the interaction with *p*-quinone follows the usual pathway and leads to the traditional 1,4-adducts, observed in the majority of reactions.

3. Reactions of Phosphoranes with Quinones

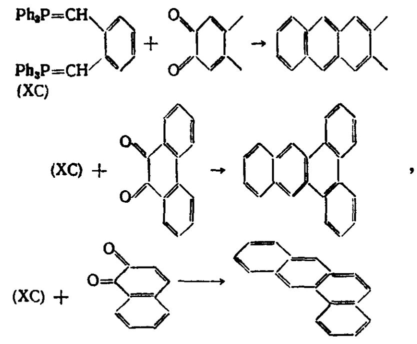
The quinonemethides (LXXXVI) are formed as intermediates in the reactions of alkylidenetriphenylphosphoranes with *o*- and *p*-quinones. They react with the initial phosphorane and give rise to the unstable betaines (LXXXVII). Depending on the substituents of the phosphorane component and in the ring, the betaines (LXXXVII) are either converted into the tautomer (LXXXVIII) or undergo the Hofmann degradation with formation of the olefin (LXXXIX):[121]



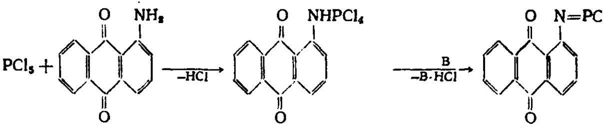
(LXXXVI) (LXXXVII)

R = COOMe, Ph; X = Cl, Ph; n = 2, 4. (LXXXVIII) (LXXXIX)

The reaction of *o*-phenylenebismethylenephosphorane (XC) with *o*-quinones can be used as a method of single-stage synthesis of complex carbocyclic aromatic compounds:[122]



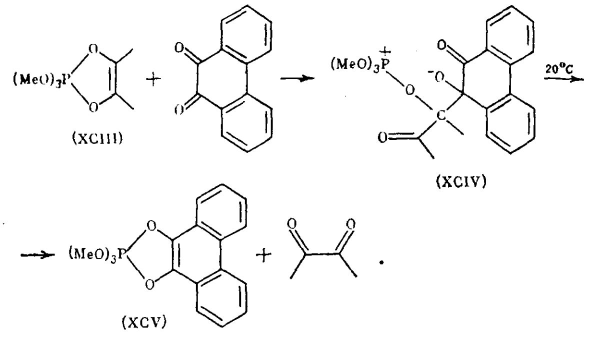
The interaction of phosphorus pentachloride with 1-aminoanthraquinone is of interest. It results in the formation of *N*-tetrachlorophosphoranyl-1-amino-anthraquinone (XCI)—a crystalline substance, which does not change after prolonged storage:



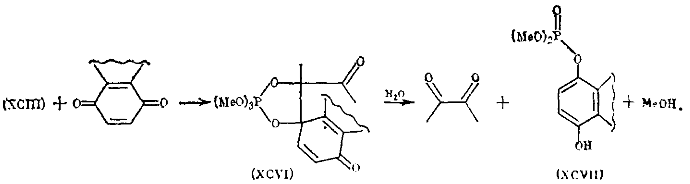
(XCI) (XCII)

Aminotetrachlorophosphoranes of the type RNHPCl$_4$ had been postulated earlier as intermediates in the reactions involving the phosphorylation of a wide variety of amines by phosphorus pentachloride. However, they were not isolated in a pure state. *N*-Tetrachlorophosphoranyl-1-aminoanthraquinone is the first representative of such compounds. Its stability may be associated with stabilisation by an intramolecular hydrogen bond. On treatment with tertiary bases, the phosphorane (XCI) is converted into trichlorophosphazoanthraquinone (XCII).[123]

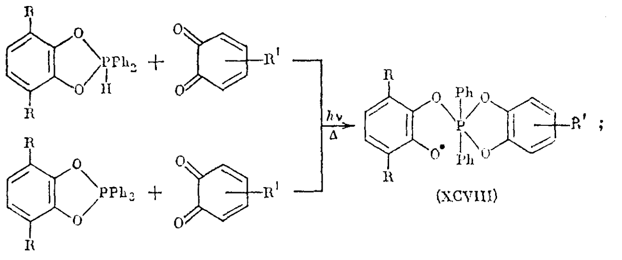
The dioxaphospholen (XCIII), obtained by the reaction of trimethyl phosphite with diacetyl, is capable of reacting with phenanthrenequinone. It has been suggested that the phospholen (XCIII), which exhibits a high phosphorylating activity, attacks the carbonyl group of phenanthrenequinone, which results in the formation of the dipolar adduct (XCIV).[124] At 20 °C, the adduct (XCIV) decomposes and the final products of reaction are diacetyl and the phosphorane (XCV):



The reaction of the phospholen (XCIII) with *p*-quinone leads to the formation of the phosphorane adducts (XCVI), which are unstable above 20 °C and whose hydrolysis affords p-hydroxyaryl dimethyl phosphates (XCVII):[124,125]



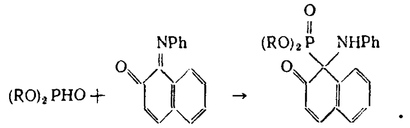
The interaction of [3,6-di(t-butyl)-1,2-phenylenedioxy]-diphenylphosphorane with *o*-quinones on exposure to UV radiation, gives rise to the radical species (XCVIII), which has also been obtained in reactions with participation of [3,6-di(t-butyl)-1,2-phenylenedioxy]triphenylphosphorane:[126]



R = t-Bu.

It follows from the data examined that the reactions of phosphorus-containing reagents with quinones and quinonoid systems frequently lead to non-trivial and sometimes unexpected results. The knowledge of such reactions undoubtedly enriches theoretical organic chemistry, opens up new ways to the synthesis of compounds with unique structures which had been hitherto inaccessible, and also provides unlimited possibilities for obtaining a wide variety of substances with properties of practical value: polymeric materials, biologically active compounds, and medicinal preparations.

During the preparation of the manuscript for printing, several interesting publications devoted to the interactions of organophosphorus compounds with quinones appeared in the literature. The results of a study of the reactions of dialkyl phosphites with sterically hindered *p*-quinones have been described.[127,128] The interaction takes place with the addition, usual in such cases, in the 1,6-positions of p-quinone with formation of adducts having the phosphate structure. An unusual reaction of dialkyl phosphites with the monoanil of *o*-naphthoquinone has been discovered.[129] Instead of the expected addition via the system of conjugated bonds of the anil X= C–C =Y, where X = C, O, or N and Y = O or N, with formation of phosphates, the reaction involving the rupture of the C=N bond and leading to the formation of adducts with the phosphonate structure takes place:



An analogous C=N bond rupture with retention of the remainder of the molecule has been found in the interaction of dialkyl phosphites with the anil of a sterically hindered quinone.[128] Radical processes with participation of quinonoid and phosphorus-containing reagents have been investigated in two studies.[130,131] Lawesson reported a new reaction of the "Lawesson reagent", which is popular in the chemistry of organophosphorus compounds at the present time. On reaction with substituted and unsubstituted p-quinones of the benzene, naphthalene, and anthracene series, it forms in certain cases phosphorus- and sulphur-containing cyclic products of a new type.[132] It has been shown[133] that the hydrazides of phosphoric acids react with p-benzoquinone in two ways: with formation of oxidation-reduction and condensation products. The operation of a particular reaction pathway depends on the expermental conditions.[133] The products of the interaction of phosphorus pentachloride with p-benzoquinone have been described.[134]

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Modern Asymmetric Synthesis of α-Aminoacids

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The principal aspects of the asymmetric synthesis of α-aminoacids with a large variety of structures are surveyed and the questions of the appearance of asymmetric induction as a result of the chirality of the catalyst, the initial compound, the reagent, or the leaving group are discussed. Studies carried out in recent years using chiral reagents capable of being regenerated and catalytic methods are examined in detail. The asymmetric reactions of α-aminoacids and other methods of synthesis are discussed briefly. Examples of the synthesis of aminoacids from chiral compounds without involving the chirality centres are not considered.

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I. INTRODUCTION

Aminoacids are widely distributed in nature and more than 500 have been discovered hitherto.[1] Despite the wide variety of the existing methods,[2,3] the search for new ways of synthesising α-aminoacids (AA) remains of current inerest, racemic AA being usually synthesised from readily available compounds under conditions ruling out multistage reactions,[4] for example:

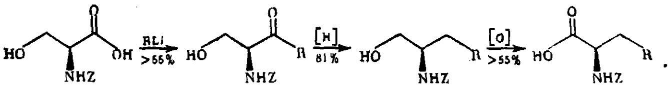
$$PhCH_2Cl + MeCONH_2 + MeCOBu \xrightarrow[Co_2(CO)_8,\,110°]{H_2,\,CO} (R,\,S)\text{-Phe}.$$

The development of the asymmetric synthesis of AA in recent years was dictated, on the one hand, by the need arising from the synthesis of natural products containing chiral carbon atoms with a AA fragment, and, on the other hand, by the necessity to develop the asymmetric synthesis of simple AA from available compounds using chiral reagents or catalysts capable of being regenerated.

Optically active AA are nowadays widely used as chiral synthons—chiral units—for the preparation of physiologically active substances,[5-7] including antiobiotics.[8] The application of AA successfully supplemented the use of carbohydrates[9,10] for the synthesis of natural products with a complex structure and, in contrast to carbohydrates, usually the entire AA molecule is employed without degradation. Furthermore, in view of their simpler structure, AA are usually available in the form of both stereoisomers. A large number of reactions involving the formation of a new chiral centre, induced with the aid of AA, are also known. Thus AA and their derivatives are used as cocatalysts of asymmetric reduction, the aldol reaction, and the Strecker synthesis.[11,12] The employment of polyaminoacids makes it possible to simulate successfully the action of enzymes. For example, the epoxidation of chalcones by hydrogen peroxide in the H_2O–CCl_4–poly-AA system has been carried out with an optical yield up to 96%.[13]

The reviews on the chemical asymmetric synthesis of AA [3,14,15] deal mainly with old studies concerned with the development of classical methods. The synthesis of AA has been partly considered in a number of reviews[15-20] and in monographs.[21,22]

We shall examine the principal aspects of the asymmetric synthesis of AA, elucidating whenever possible the causes of asymmetric induction, concentrating attention on syntheses using chiral reagents capable of being regenerated and on catalytic methods. Examples of asymmetric transformation without the involvement of the centre of chirality, as in the synthesis of (R)-AA from (S)-Ser [23] (see the scheme below) will not be discussed.



(S)-Ser (B)-AA

The questions of micellar catalysis and the use of enzymic reactions and their combinations with chemical methods for the synthesis of optically active AA have already been considered.[24-26]

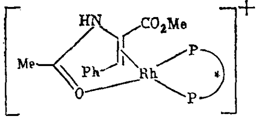
Asymmetric synthesis is the term applied to a process in which a prochiral molecule or its fragment is converted into a chiral molecule with unequal amounts of stereoisomeric products.[27] The process proceeds under the influence of a chiral reagent, the chiral component of the initial molecule, or a chiral catalyst. The interaction of the chiral and prochiral molecules inevitably results in the formation of intermediate diastereoisomeric compounds and (or) diastereoisomeric transition states, the energy difference between which actually determines the ratio of the diastereoisomers or enantiomers formed. This result is estimated in practice in terms of the diastereoisomeric (enantiomeric) excess of the reaction products or the optical yield (OY):

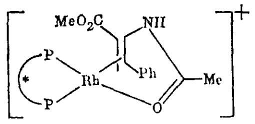
$$p = \mathrm{OY} = \left|\frac{[S]-[R]}{[S]+[R]}\right| \cdot 100\,\% = \frac{[\alpha]_{\mathrm{obs}}}{[\alpha]_{\mathrm{pure}}} \cdot 100\,\% \ .$$

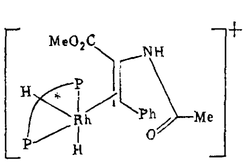
The aim of the asymmetric synthesis is to carry out the reaction with the maximum value of p for which it is sufficient to have low values of $\Delta\Delta G$, comparable to the energy of rotation about the C–C bond:

$\Delta\Delta G$, kcal mol^{-1}	0.82	1.30	1.74	2.72
p, %	60	80	90	98

Kinetically and thermodynamically controlled asymmetric syntheses are distinguished. The most striking example of kinetic control is the asymmetric reduction of *N*-acyldehydroaminoacids or chiral phosphinerhodium catalysts, where the activity of the minor intermediate diastereoisomer (I) [its content does not exceed 5% relative to compound (II)], which is higher by a factor of 10^2–10^3, determines the stereochemical course of the process and the formation of the diastereoisomer (III) with $p \geq 95\%$ [28] (Fig. 1).


(I)


(II)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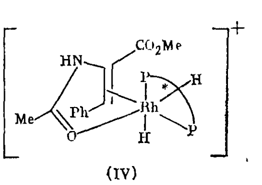
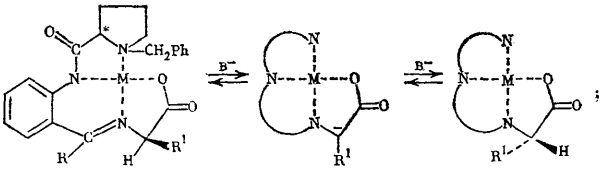

(IV)

As an example of thermodynamic control, we may quote the retroracemisation of the aminoacid fragment in transition metal complexes (V) of Schiff bases derived from chiral carbonyl compounds.[29–31] As a result of the epimerisation of the α-carbon atom of the aminoacid fragment, the mixture of the complexes (V) and (VI) formed initially is converted via compound (VII) into an equilibrium mixture with the ratio (V)/(VI) up to 10 : 1. After the decomposition of the mixture, AA with *p* up to 90% are isolated:



(V) (VII) (VI)
M = Ni, Cu; R = H, Me Ph; R^1 = Me, iso-Pr, Ph, CH$_2$Ph etc.

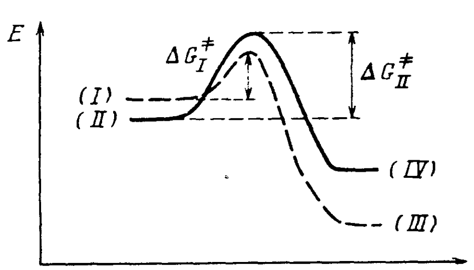
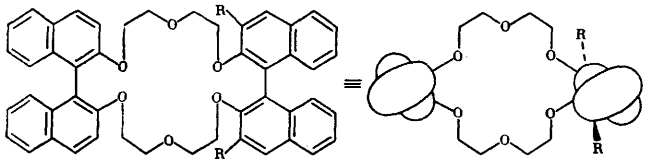


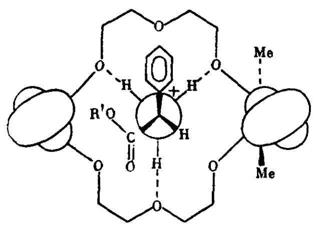
Figure 1. The energy diagram for the stage involving the formation of the rhodium hydride complex.[28]

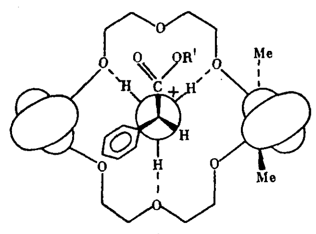
In most studies on the synthesis of AA, only the reaction result (the optical yield) is considered, without elucidating the causes of the asymmetric induction. Its manifestation is usually explained from stereochemical standpoints,[32] although the influence of electronic factors has also been demonstrated in a number of instances.

II. CHIRAL RECOGNITION AND TRANSPORT OF AMINOACIDS

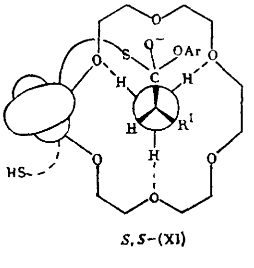
The success of asymmetric synthesis is associated with the elucidation of the nature and extent of the chiral recognition in complexes of aminoacid enantiomers with chiral compounds. Crown ethers are known to form readily 1 : 1 complexes with AA.[33] The complex-forming properties of crown ethers in relation to ammonium ions have attracted attention in view of their similarity to natural ionophores—antibiotics capable of binding metals, biologically important amines, and AA.[34] The chiral recognition of amines and AA by chiral crown ethers of type (VIII) with binaphthyl fragments,[35–38] spiro-crown ethers,[39] pyridinocrown ethers,[40] various crown and aza-crown compounds,[41,42] and other compounds[34,43] has been studied recently. Thus the diasteroisomers (*S*,*S*,*S*)-(IX) and (*S*,*S*,*R*)-(X) have been obtained from salts formed by AA esters with acids and from compound (VIII). The experimental value of ΔΔ*G* (up to 2 kcal mole^{-1}) is actually related to the difference between the interactions of the chiral binaphthyl fragments with H or the CCOR′ group:[44]

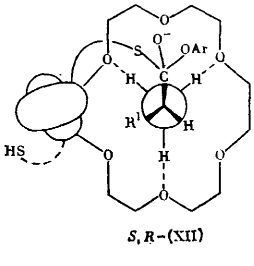

R = H, Me (VIII)


(*S*,*S*,*S*)-(IX)


(*S*,*S*,*R*)-(X)

The enantioselective thiolysis of the *p*-nitrophenyl esters of AA (AA–OAr) on treatment with an analogue of compound (VIII) containing one binaphthyl fragment with the group R = $CH_2OC_6H_4SH$ is an example of the reaction with esters of type (VIII) whose stereoselectivity can be explained by considering molecular models of the intermediate complex.[36] Comparison of the structures of (*S*,*S*)-(XI) and (*S*,*R*)-(XII) indicates that the complex (XI) is preferable because of the interaction of the chiral barrier with the hydrogen atom and not with an alkyl group of the AA, as in the case of compound (XII). This explains satisfactorily the difference between the relative thiolysis rate constants; the ratio of the constants increases from 1 to 8.3 and 9.2 respectively with increasing bulk of the side chain on passing from Ala to Phe and Val.


S,*S*-(XI)


S,*R*-(XII)

The transport of AA through synthetic and natural membranes, which takes place stereoselectively in living organisms through lipophilic cell membranes, is associated with the phenomenon of recognition.[44] A number of biomimetic systems—crown ethers,[35,44] their spirobiindan derivatives,[45] and azacrown ethers[34]—have been developed for the selective transport of one of the enantiomers of the AA esters in the form of the hydrochloride. The transport is from one aqueous phase to another via a liquid membrane made up of a layer of organic solvent containing the chiral transferring agent. The cation associated with the given compound, for example Na$^+$, is transported in the opposite direction simultaneously with the transport of the AA salt. The driving force of the process is the entropy of solution and the change in the solvation energy when an inorganic salt is replaced by an organic salt. The use of (*S,S*)-(VII, R = Me) in the cell (Fig.2) made it possible to isolated (0 °C, 22 h) (*S*)-PGly-OMe with *p* up to 86% in the right-hand limb from the racemate in the left-hand limb, while the use of (*R,R*)-(VIII) affords (*R*)-PGly-OMe with *p* up to 90%. $\Delta\Delta G$ reaches 1.96 kcal mol^{-1} for p-HO–PGly–OMe [40] and −2.15 kcal mol^{-1} for Phe–OMe.[35] Such high results have so far been obtained only for AA esters. The study of the transport of free AA has so far yielded low values of *p*, which depend greatly on the experimental conditions.[34,46] The PGly enantiomers with *p* = 91.6% have been separated by means of a liquid membrane containing a chiral crown ether and a polymer.[47]

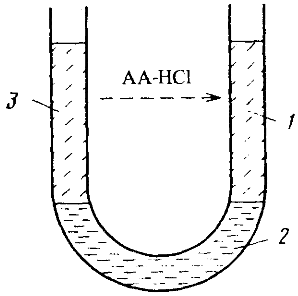
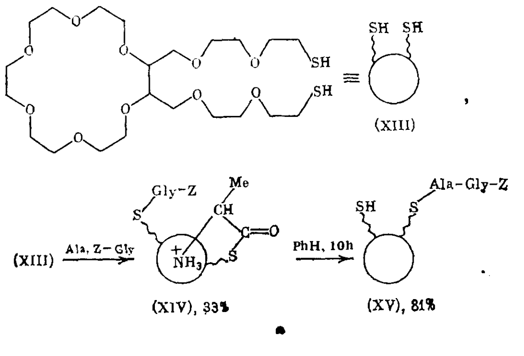


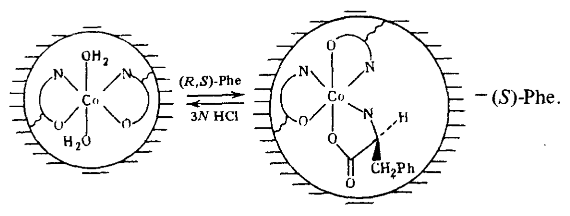
Figure 2. Cell for the phase-transfer enantioselective transport of aminoacid esters:[35] 1) 0.1 M HCl; 2) 0.027 M solution of (*S,S*-)- or (*R,R*)-(VIII) in $CHCl_3$; 3) aqueous solution of 0.08 M HCl, 0.08 M $LiPF_6$, and 0.05–0.08 M AA.HCl.

Crown ethers (XIII) with functional groups have been used as models of enzymes in the synthesis of peptides[48] (Scheme 1). The reaction involves the usual stages of peptide synthesis: the formation of a covalent intermediate, followed by the catalytic complex (XIV), and the reaction of the latter with the second substrate and the formation of the product (XV).

Scheme 1



A specific chiral environment can be created for the purpose of the recognition of AA enantiomers also by local synthesis, for example, by the copolymerisation of the cobalt(III) complex of (*R*)-Phe, containing a number of chiral groups and activated double bonds, with styrene and divinylbenzene:[50]



The polymeric gel obtained retains its initial structure of a "chiral lacuna" after hydrolysis, because, as a result of treatment with an excess of (*R,S*)-Phe, it forms preferentially a complex with (*R*)-Phe (*p* = 74%).

The diasteroisomeric interactions with AA are extremely varied. There is a possibility of the chiral recognition of N-Ac-PGly and N-Ac-Phe as a result of the formation of diastereoisomer solvates with tartaric acid derivatives via the formation of hydrogen bonds.[51] The study of chiral recognition in the formation of complexes with esters of (*R*)-, (*S*)-, and (*R,S*)-*N*-[4(1-pyrenyl)butanoyl]tryptophans in methanol and optically active octanols showed that it is associated with the differences between electrostatic, dispersion, and resonance interactions.[52]

Examples of the chiral recognition of prochiral substrates as a result of diastereoisomeric interactions, which are used for the asymmetric synthesis of AA, will be examined below.

III. ASYMMETRIC REACTIONS OF AMINOACIDS

The asymmetric transformations, sometimes referred to as *anti*- or *retro*-racemisation, include, in the stage determining the stereochemistry of the process, the inversion of the configuration of the α-carbon atom of the AA, which justifies their consideration in this review.

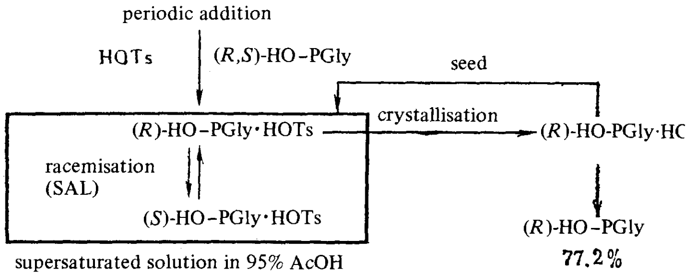
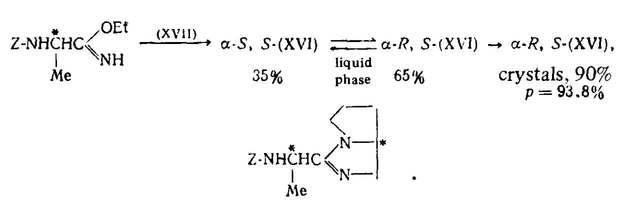


Figure 3. Schematic illustration of the asymmetric transformation of toluene-p-sulphonate of (*R,S*)-p-hydroxyphenylglycine.55

The conditions in the asymmetric transformations of *N*-Ac-Leu, *N*-butyroyl-Pro, *N*-benzoyl-PGly,[53] Ala and PGly,[54] and p-HO-Pgly [55] have now been worked out in detail. The essential feature of these transformations is a combination of the preferential crystallisation of one of the enantiomers in saturated solutions of the racemate with the racemisation of the other enantiomer. Thus a supersaturated solution of *N*-Ac(*R*,*S*)-Leu in acetic acid with catalytic amounts of acetic anhydride was cooled at a rate of 10 K h^{-1} from 100° to 40 °C after the addition of crystals of the (*S*)-isomer as a seed. This resulted in the formation of almost optically pure (*S*)-*N*-Ac-Leu in 70% yield relative to the initial racemic mixture.[53] The toluene-p-sulphonate salts of (*R*,*S*)-p-HO-PGly-[(*R*,*S*)-HO-PGly.HOTs] are racemised using 95% of acetic acid and a catalytic amount of salicylaldehyde (SAL) [55] (Fig.3).

The use of the faster racemistation of intermediate Schiff base derived from the ester (*R*,*S*)-PGly compared with the ester of one of the PGly enantiomers, which accumulates in solution, in the presence of (+)-tartaric acid affords, as a result of the asymmetric transformation of the second kind, the pure (*R*)-enantiomer in 85% yield.[56] The transition from (*R*,*S*)-Ala to (*R*)-Ala via the readily epimerising imidazolines (XVI), obtained using (*S*)-2-aminomethylpyrrolidine (XVII), has been achieved:[57]

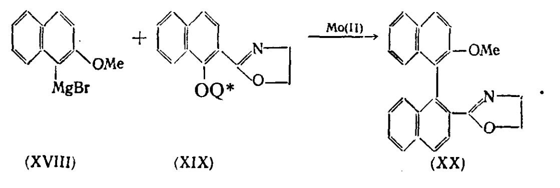


(XVI)

By combining the epimerisation and preferential crystallisation of the complex with $NiCl_2$, the asymmetric transformation of α-amino-ε-caprolactam (a precursor of lysine) has been carried out analogously in 50% yield (p = 96%).[58] The asymmetric transformations of AA via the intermediate formation of chiral complexes of Schiff bases with transition metals[29] are considered in Section VI.

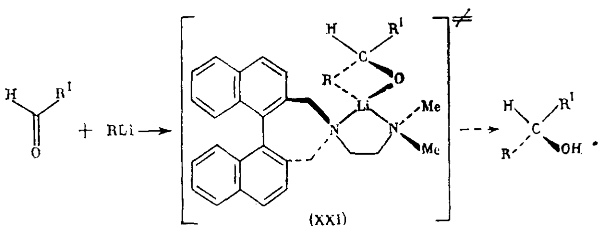
IV. ASYMMETRIC INDUCTION BY THE CHIRAL LEAVING GROUP

Asymmetric protonation or alkylation of carbanions by chiral electrophiles is also included in the electrophilic asymmetric synthesis of AA after asymmetric transformations.[59] An example of the asymmetric induction by the leaving group in the nucleophilic aromatic substitution using 2-methoxy-1-naphthylmagnesium bromide (XVIII) as the nuclophile and the quininoxy-group (OQ*) as the leaving group in the electrophile (XIX) is known.[60] The yield of the product (XX) reached 88% (p = 95%):



(XVIII) (XIX) (XX)

This result can be explained by the intermediate formation of two diastereoisomeric chelates with Mo^{2+}, ΔΔG reaching 2.4 kcal mol^{-1}. Induction by chiral lithium amides can be achieved analogously, for example, in the catalysis of the addition of alkyl-lithium to aldehydes via compound (XXI) with formation of alcohols (yield 35–75%, p = 23–95%):[61]

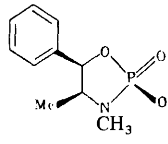


(XXI)

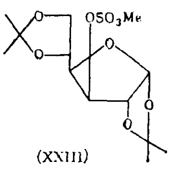
A rare instance of the use of electrophilic asymmetric amination for the synthesis of AA from the chiral reagent (XXII), prepared for (−)-ephedrine, has been described:[62]

$$Ph\bar{C}RCOOEtLi^+ \xrightarrow{(-)\text{-(XXII)}} Ph\overset{*}{C}R\,(COOEt)\,NMe_2\,;$$

R = H (yield 50%, p = 23%); R = Me (yield 56%, p = 21%);

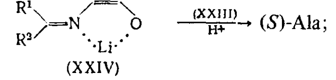


(−)-(XXII)



(XXIII) .

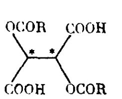
The enantioselective alkylation by compounds (XXIII) of lithium enolates obtained from a Schiff base of the glycine ester (XXIV) has been reported recently:[63]



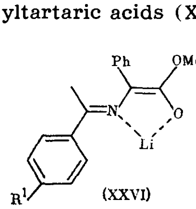
(XXIV)

R^1	H	iso-Pr	Ph	p-$NMe_2C_6H_4$	p-$NMe_2C_6H_4$
R^2	Ph	iso-Bu	t-Bu	t-Bu	adamantyl (Ad)
Yield of (*S*)-Ala, %	50	69	72	70	90
p, %	0	35	61	66	71

The result obtained is explained by the intermediate coordination of the enolate (XXIV) to the chiral alkylating agent (XXIII), which hinders the attack on the double bond from the *re*-side, the hindrance increasing with increasing bulk of the substituents in compound (XXIV). Asymmetric protonation for the synthesis of AA has been developed in detail.[59] The essential feature of the method consists in the protonation of the lithium enolates of the Schiff bases derived from AA esters by chiral acids, which are usually (2*R*, 3*R*)- or (2*S*, 3*S*)-diacyltartaric acids (XXV):



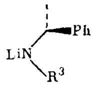
(XXV)



(XXVI)

$LiN(R^2)_2$

(XXVII)



(XXVIII)

As a consequence of the high coordinating capacity of lithium in relation to the electron-donating atoms, the product is the *syn*-enolate (XXVI), whose protonation by (*R*)- or (*S*)-(XXV) under the conditions of kinetic control affords AA enriched in one of the enantiomers. It has been established in relation to the transformations in PGly (Table 1) that the stereoselectivity increases with increasing bulk of the substituents in the amide and the acid and also with enhancement of the electron-donating character of the group in the aromatic ring of the Schiff base, which leads to the formation of a "harder" enolate. For all the AA investigated (Ala, Trp, Leu, Phe, Val, Met, PGly, NLe), the protonation of the enolate of type (XVI) by treatment with (2*R*, 3*R*)-(XXV) yielded the (*S*)-product,[59] while the chiral acids were recovered without loss of optical activity. On double asymmetric induction using (*R*)-(XXVIII), *p* increases to 70% with a chemical yield of 90%. In the case of chiral aminocarbonyl compounds, protonation by the derivatives (XXV) proceeds with p up to 92%.[66] According to Duhamel et al.,[59] it can be used for the transformation of carboxylic acids, ketones (via enamines), allyl alcohols (via α-hydroxyketones), allyl halides (via α-halogenoketones), etc. Asymmetric protonation can be achieved also without the loss of the chiral group; for example, the reaction of phthalimido-t-butylketen (XXIX) with an (*R*)-Ala ester, results in the formation of the (*R*,*R*)-dipeptide with *p* = 70%:[67]

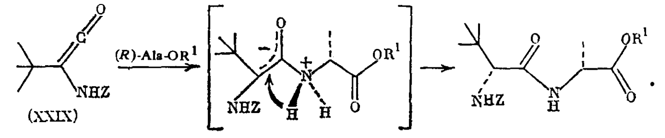


Table 1. The influence of substituents on the optical yield of (*S*)-PGly in the reaction of compound (XXV) with the enolate (XXVI).[59,63–65]

R in (XXV)	*p*, % (R¹=H)*	R¹ in (XXVI)	*p*, % (R = t-Bu)*	R² in (XXVII)	R³ in (XXVIII)	*p*, % (R¹ = H, R = t-Bu)*	(XXV)	*p*, % (R¹ = H, R = t-Bu, R² = Et)
Me	2.6	CN	12	C_6H_{11}	—	35	2*R*, 3*R*	70
iso-Pr	12	Cl	31	Et	—	28	2*S*, 3*S*	5.5
t-Bu	50	H	50	iso-Pr	—	50	*meso*-	24
t-$BuCH_2$	16	Me	53	—	Me	60	racemate	39
	54	MeO	57	—	Et	70	—	—
Ad	—	Me_2N	61	—	—	—	—	—

*The reaction was carried out with (2*R*,3*R*)-(XXV).

The asymmetric protonation method can be developed further using chiral polyacid. The protonation of chiral anions by achiral acids has been investigated more widely and is examined below.

V. ENANTIOSELECTIVE REACTIONS OF CARBANIONS

In recent years notable advances have been made in the asymmetric synthesis involving the enantioselective formation of C–C bonds.[68] Stabilised carbanions, which exist in the form of metal complexes are frequently used for this purpose, the complexes being obtained from carbanion compounds, for example, α-alkyl-β-ketoesters,[69] α-hydroxyesters,[70] or nitrogen-containing compounds—hydrazones[71,72] or amidines.[73] The enantioselective alkylation of such carbanions proceeds with a high value of *p*.

AA are frequently obtained by alkylating the chiral Schiff bases (XXX) derived from the simplest AA, which can be readily synthesised from chiral carbonyl compounds and AA esters.[79] The use of the Schiff bases increases the CH acidity of the aminoacid fragment of the AA [80] and makes it possible to carry out reactions even with weak electrophiles (alkyl halides), ensures the ready regeneration of the chiral carbonyl compound $(R^1)^*{=}O$, and leads to comparatively high values of p (Table 2):

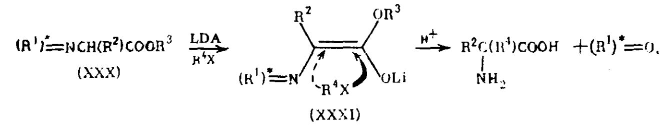
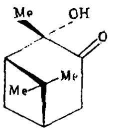


Table 2. Alkylation of chiral Schiff bases (XXX).

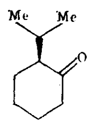
Chiral reagent, $(R^1)^* = 0$	R²	R³	R⁴	Yield of AA, %	*p*, %	Refs.
(XXXII)	H	t-Bu	Me	52	83	[74]
	H	t-Bu	n-Pr	50	83	[74]
	H	t-Bu	$PhCH_2$	79	72	[74]
	H	t-Bu	$3,4\text{-}(HO)_2C_6H_3CH_2$	62	66	[74]
	H	Me	$(CH_2)_6CH{=}CH_2$	40	95	[75]
(XXXIII)	Me	t-Bu	$3,4\text{-}(HO)_2C_6H_3CH_2$	74	24	[76]
	Me	t-Bu	$PhCH_2$	55	21	[76]
(XXXII)	Me	Me	n-Pr	81	83	[77]
	Me	Me	$CH_2C{\equiv}CH$	78	52	[77]
	n-Pr	Me	Me	87	90	[77]
	n-Pr	Me	$CH_2CH{=}CH_2$	70	15	[77]
(XXXIV)	H	t-Bu	PhCHOH	67	64*	[78]
	H	t-Bu	*o*-MeC_6H_4CHOH	67	70**	[78]
(XXXV)	Me	Me	$PhCH_2$	83	83	[79]
	Me	Me	$CH_2CH{=}CH_2$	85	85	[79]
	Me	Me	$CH_2CH{=}CHPh$	65	60	[79]

threo : *allo* = 3 : 1.
***threo* : *allo* = 12 : 1.

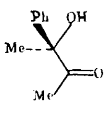
The Schiff base is deprotonated, for example, with lithium diisopropylamide (LDA) in tetrahydrofuran (THF) to give the enolate (XXXI), which is alkylated with alkyl halides, the use of the (*S*)-reagent $(R^1)^*$ giving rise to an excess of the (*R*)-product. Asymmetric induction can be achieved for achiral Schiff bases by means of chiral lithium amides obtained from (*S*)-Pro or (*S*)-Leu, but *p* does not exceed 31%.[81] The induction is also weak when the chiral centre is moved away from the α-carbon atom of the AA by employing menthyl esters, whose derivatives afford, after deprotonation and alkylation, AA in yields of 90% and *p* = 5–55%.[82] A 48% yield of (*S*)-Ala is reached when the menthyl ester of isocyanic acid is metallated.[83] The use of other AA derivatives, for example, *N*-formyl-*N*-alkylaminoacetonitrile, likewise produces low values of *p*.[84]



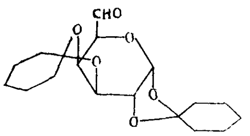
(XXXII)



(XXXIII)



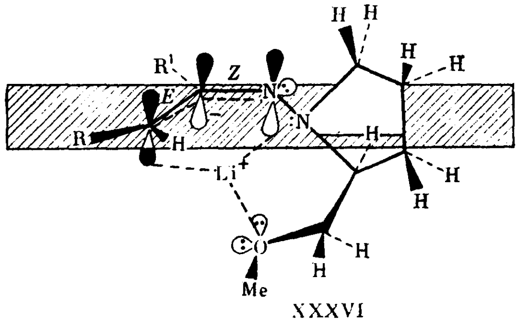
(XXXIV)



(XXXV)

In another alkylation method, proposed by Enders[85] and used to synthesise AA,[71] one begins with lithiohydrazones or lithioamidines derived from (*S*)-1-amino-2-methoxymethylpyrrolidine. The structure of the lithio-derivatives of hydrazones has not been accurately established, in contrast to that of lithium enolates. The structure (XXXVI) (Fig.4) has been proposed from spectroscopic data and confirm by an MNDO calculation. The result of the electrophilic substitution of the Li^+ ion is determined by the rotation about the N–N bonds if it is assumed that the negative end of the dipole of the electrophile forms a complex with the Li^+ ion.

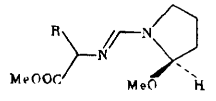
Since the electrophile attacks the anion (XXXVI) from below with formation of an (*R*)-product, then, for the more favourable *NN*-conformation in compound (XXXVI), *syn*-substitution takes place in relation to lithium. These features can be attributed also to electrophilic substitution in the amidines (XXXVII), where the preferential formation of the (*S*,*R*)-product is associated with the preferential *syn*-substitution of the lithium complex, which yields (*R*)-AA with p = 15 to 51%.[71] The result of the alkylation of enolates obtained from Schiff bases (XXXI) can be explained analogously.



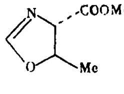
XXXVI

Figure 4. The structure of the lithio-derivative of the hydrazone (XXXVI).[85]

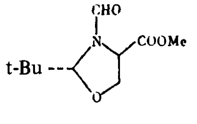
Rigid cyclic systems give rise to better results than their linear analogues. Thus the alkylation of the carbanion obtained from derivatives of the chiral 1,4-benzodiazepin-2-one yielded an AA with p up to 85%.[86] The advantages of the use of cyclic systems have been demonstrated particularly strikingly in two general methods of synthesis of a whole series of AA, developed by Seebach et al.[87] and Schöllkopf;[88,89] in both cases, the rigid chiral carbanion is attacked by the electrophile with an exceptionally high diastereoselectivity. The method of "self-reproducing chirality", proposed by Seebach, consists in effecting 1,3-asymmetric induction; it is convenient for the synthesis of α-C derivatives of the AA for which direct formation of enolates is impossible owing to β-elimination: Ser,[90] Thr,[91] Cys,[92,93] and Pro.[87] The principal feature of the method is the synthesis of chiral enolates from optically pure cyclic products: substituted oxazolines (XXXVIII) for Thr, oxazolidines (XXXIX) for Ser, and bicyclic compounds of the type (XL) for Pro and Cys:



(XXXVII)



(XXXVIII)



(XXXIX)

As shown in Scheme 2 for the adduct (XL, Y = CH_2),[87] the nucleophilic centre of the enolate is attacked by all kinds of electrophiles (D_3O^+, alkyl halides, carbonyl compounds, and alkenes) with restoration of the initial chiral centre and the formation of virtually only one of the possible diastereoisomers even in the case of three chiral centres (Table 3).

Scheme 2

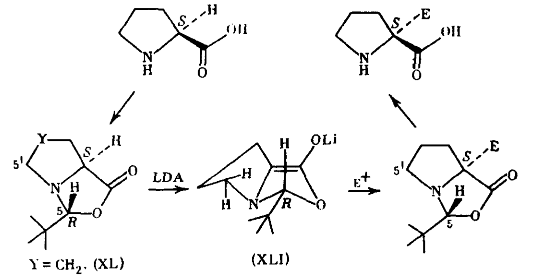
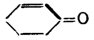
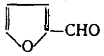
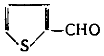


Table 3. The interaction of enolates obtained from compounds (XXXVIII), (XXXIX), and (XL) with electrophiles.

Initial compound	Electrophile	Reaction product		Refs.
		yield, %	p, %	
(XL), Y = CH_2	MeI	93	95	[87]
	$PhCH_2Br$	91	95	
	$MeCOOCH_2Br$	40	95	
	PhCHO	72	94	
	MeCHO	88	94	
	Me_2CO	93	95	
	$MeCOCH_2COOMe$	62	51	
		50*	95	
	»	21**	95	
(XXXIX)	$PhCH_2Br$	52	99	[90]
	MeOD	71	98	
	Me_2CO	58	99	
	PhCHO	70	99	
(XXXVIII)	MeI	94	93	[94]
	$PhCH_2Br$	93	99	
	Me_2CO	68	99	
(XL), Y=S	PhCHO	64	92	[93]
	p-$MeOC_6H_4CHO$	68	96	
		45	88	
		44	94	
	PhCH=CHCHO	48	89	

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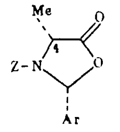
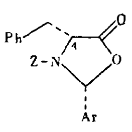
*1,2-Addition. **1,4-Addition.

The stereochemical result is because the electrophile does not distinguish kinetically the two sides of the chiral enolate (XLI) obtained from the adduct of (*S*)-proline with pivalic aldehyde (XL). The formation of compound (XL) is rigorrously distereoselective, because the existence of the (*S*,*S*)-diastereoisomer is unfavourable—in this case the pseudoaxial t-Bu group is in the eclipsed conformation relative to the 5′-CH_2 group of the pyrrolidine ring. The enolate (XLI) is formed with disappearance of the initial centre of chirality *S*-(2) and retention of the new centre *R*-(5). Presumably the Li^+ ion is coordinated to the oxygen of the enolate preferentially from the *re*-side of the plane (from below) in order to reduce the extent of the non-bonding interactions from the side of the pseudoaxial H(5) and the pyrrolidine fragment. This should lead to attack by the electrophile coordinated to the Li^+ ion from the *re*-side and the restoration of the initial centre of chirality *S*-(2), which has in fact been observed. The high stability of the carbanion (XLI) makes it possible to carry out also the Michael reaction, for example, with cyclohexenone, whereupon adducts with $p = 95\%$ are produced.[87] The method has been extended to Ala and Phe by converting them into chiral cis-2-aryl-2-benzyloxycarbonyloxazolidinones (XLII) and (XLIII); the alkylation of their potassium enolates at C(4) by treatment with MeI and $PhCH_2Br$ afforded (*R*)- or (*S*)-α-Me-Phe after alkaline hydrolysis with hydrogenolysis.[94]

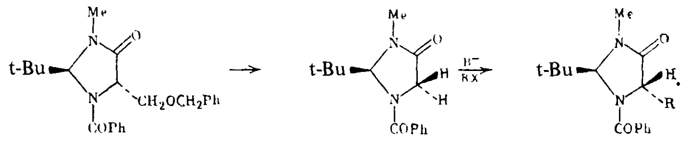


(XLII)



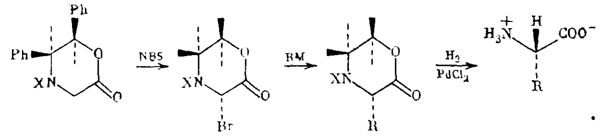
(XLIII)

The method is applicable to the synthesis of natural AA from other AA. (*S*)-β-*O*-benzyl-Ser was converted on interaction with pivalic aldehyde into the *trans*-imidazolidinone (XLIV), which gives rise, after oxidation and decarboxylation, to the imidazolidinone (XLV) containing the Gly fragment. The alkylation of its chiral enolate with MeI or $PhCH_2Br$ (produced the (2*S*, 5*S*)-imidazolidinones (XLVI) in 51 and 45% yields respectively for $p = 95\%$:[95]



(XLIV) (XLV) (XLVI)

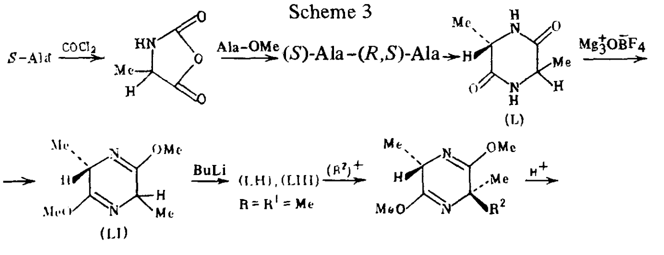
The attempts to obtain the enolate from the chiral lactone (XLVII) were unsuccessful, but the generation of an electrophilic centre by passing to compound (XLVIII) made it possible to carry out the reactions with various nucleophiles, leading to the lactone (XLIX), and to isolate the AA [(*S*)-Ala, (*S*)-NVa, (*S*)-NLe, etc.]:[96]

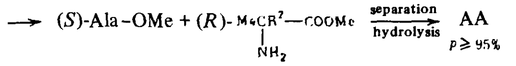


(XLVII) (XLVIII) (XLIX) $p > 96\%$

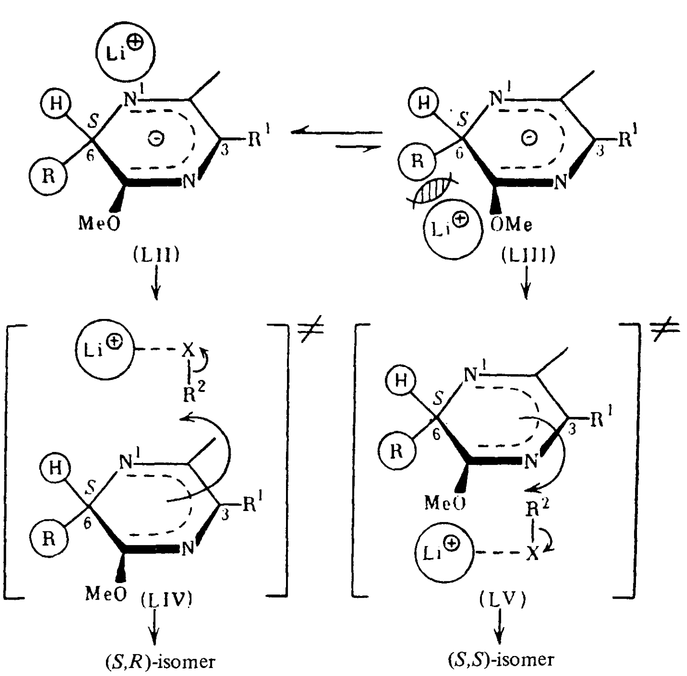
The alkylation of Asp, via acyclic enolates, gave $p = 60\%$.[97] In Schöllkopf's method,[88,89] one initially synthesises the dioxopiperazines (L) from Gly or the available racemic AA (for example, Ala) and a chiral reagent—(*S*)-Ala, (*S*)-t-Leu, (*S*)-Val, or (*S*)-α-Me-3,4-$(MeO)_2$Phe. The dioxopiperazines are alkylated to give the bislactim ethers (LI), which exhibit a high CH acidity and form the chiral carbanions (LII) and (LIII) (Fig.5); the latter react with a wide range of electrophiles diastereoselectively with a high *p* value. The heterocycle obtained is hydrolysed with liberation of the auxiliary chiral reagent and of a new optically active AA in the form of an ester, as shown in Scheme 3 for the reaction with cyclo-[(*S*)-Ala, (*R*,*S*)-Ala]:[93]

Scheme 3





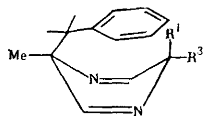
$$\longrightarrow (S)\text{-Ala-OMe} + (R)\text{-}\underset{NH_2}{\underset{|}{MeCR^2}}\text{—COOMe} \xrightarrow[\text{hydrolysis}]{\text{separation}} \underset{p \geq 95\%}{AA} .$$



R = Me, iso-Pr, t-Bu; R¹ = H, Me.

Figure 5. Schematic representation of the addition of an electrophile to the heterocyclic anion (LII)–(LIII).[88]

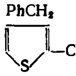
The authors assume that the dihydropyrazine anion is planar by virtue of the fulfillment of the Hückel condition and one of its diastereotopic sides is greatly shielded by the substituent R (Fig.5). It has been suggested that the Li^+ ion is close to the N(1) atom, which has the maximum electron density according to calculations. Thus the equilibrium is displaced towards compound (LII) virtue of the steric hindrance by the group R. The attack by the electrophile on the anion (LIII) is sterically hindered and the reaction proceeds mainly via the energetically more favourable state (LIV). The favourable combination of kinetic and thermodynamic factors is responsible for the high value of *p* (usually >95%). The role of the metal and the structure of the ion pairs were not discussed by Schöllkopf,[88,89,98] although he showed that the replacement of Li by a metal with shorter bonds [for example, $Ti(NMe_3)_3$] leads to greater asymmetric induction.[99] The structure of the alkylated products (LVI) and (LVII), obtained from compound (LII, R, $R^1 = Me$, $R^2 = CH_2Ph$) and corresponding to a folded conformation in which the benzene ring overhangs the heterocyclic ring, serves as evidence in support of the proposed mechanism.[89]



$R^1 = H$, $R^3 = Me$ (LVI)
$R^1 = Me$, $R^3 = H$ (LVII)

Such a structure, which is unfavourable as regards steric considerations, is realised also for cyclic dipeptides of the phenylalanine series.[100] Thus the stereoselectivity of the reactions of the chelate complexes of lithium considered in this Section is determined by the preferred introduction of the coordinated lithium atom on the *re*- or *si*-side relative to the nucleophilic centre of the anion and the subsequent electrophilic attack from the same side via the intermediate binding of lithium, which is the reason for the preferred *syn*-substitution mechanism. The knowledge and control of the steric and electronic factors in the stage determining the degree of asymmetric induction make it possible to regulate the stereoselectivity. Thus, the replacement of R = Me by R = t-Bu in compound (L) increases the stereoselectivity sharply, while the introduction of the phenyl group (R = Ph) gives rise to the opposite result.[89]

Table 4. The yields of the products of the interaction of carbanions of types (LII) and (LIII) with electrophiles.

Carbanion	R²	Yield, %	p, % *	Refs.
(LII), (LIII) R = t-Bu R¹=H {from cyclo-[(*S*)-Val-Gly]}	CH(Me)OH	—	95 (91)*	[99]
	CH(Me)OH	—	85 (63)	[101]
	$C(Me)_2OH$	—	95	[101]
	CMe(Ph)OH	—	95 (38)	[101]
	$CH(CH_2Ph)OH$	—	89 (66)	[101]
	$CH_2{=}CPh$	90	95	[102]
	CH_2Ph	81	91—95	[104]
	$3,4\text{-}(MeO)_2C_6H_3CH_2$	91	85	[104]
	$PhCH{=}CHCH_2$	90	95	[104]
	$CH_2{=}CHCH_2$	88	60—65	[104]
	$Me(CH_2)_6$	62	75—80	[104]
	$PhOCH_2$	81	93	[105]
	$MeOC(Me)_2$	80	95	[105]
	$CF(Me)_2$	46	95	[106]
	N-Boc-(3-indolyl)CH_2	83	88	[107]
	$CR(CH_2Cl)CH_2ON$	90	95	[108]
(LII), (LIII) R = t-Bu, R¹ = Me {from cyclo-[(*S*)-Val-Ala]}	CMe_2OH	94	95	[103]
	C(Me)PhOH	93	95	[103]
	N-Boc-(3-indolyl)CH_2	81	95	[107]
	$PhCH_2OCH_2$	91	95	[109]
	$PhCH_2$	68	95	[110]
	n-C_7H_{15}	43	95	[110]
	$PhCH{=}CHCH_2$	80	95	[110]
	$CH_2{=}CHCH_2$	90	95	[110]
	$Ph(CH_2)_2$	79	95	[111]
	$C[^2H]_3$	—	95	[112]
(LII), (LIII) R = R¹ = t-Bu {from cyclo-[(*S*)-t-Leu]$_2$}	Me	91	95	[113]
	$CH_2{=}CHCH_2$	78	95	[113]
(LII), (LIII) R¹ = t-Bu, R = H {from cyclo-[(*S*)-t-Leu-Gly]}	$PhCH_2O$	87	95	[114]
	n-$MeOCMe_2$	58	93	[114]
	$CH_2{=}CHCH_2$	84	93	[114]
	$CH{\equiv}CCH_2$	86	93	[114]
	t-$BuOCOCH_2$	89	93	[114]
(LII), (LIII) R = 3,4-$(MeO)_2C_6H_3$·CH_2, R¹ = H {from cyclo-[(*S*)-α-Me-3,4-$(MeO)_2$Phe-Gly]}	$PhCH_2O$	74	95	[105]
	$MeOCMe_2$	79	93	[115]
	$CH_2{=}CHCH_2$	70	80	[115]
	n-C_7H_{15}	—	85	[115]
from (LVIII)	$PhCH_2$	94	95	[116]
		87	95	[116]
	$CH_2{=}CHCH_2$	66	17	[116]
	cyclo-$C_6H_{11}CH_2$	20	35	[116]
from (LX) R = CMe_3, R¹ = 2-furyl	$PhCH_2$ ***	90	95	[117]
	Me ***	95	90	[117]
	$CH_2{=}CHCH_2$	85	95	[118]
	$PhCH_2$	92	95	[118]
	Me	92	95	[118]

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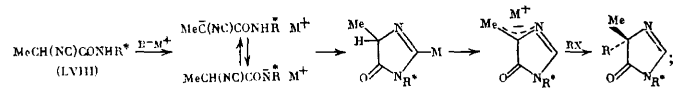
*The values of p (with respect to C(3) are indicated in brackets.

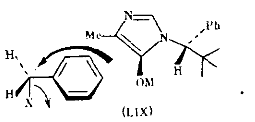
**$Ti(NMe_3)_3$ was used as the counterion.

***R^1 = Rh.

Cyclo-[(*S*)-Val-Gly] or cyclo][(*S*)-Val-Ala] is used most often in the Schöllkopf's method, which makes it possible to obtain various (*R*)-AA (Table 4). High optical yields have been achieved using (*S*)-t-Leu, which, however, is difficult to obtain.[89] Ketones also react with (LI) (p = 95%), while aldehydes react with additional induction at C′ (3), (6*S*, 3*R*, 3′*S*)-diastereoisomers being formed preferentially.[101] Dehydration leads to (*R*)-α-vinyl-Ala and (*R*)-vinyl-Gly.[102,103] Hydrolysis to the AA esters proceeds without racemisation (Table 4). The large number of stages, the long reaction time, and the difficulty of separating the AA esters lead to the formation of products in yields of only 17–24% relative to the initial AA. The alkylation of the anions of chirally 1-substituted 4-methyl-2-imdazolin-5-ones (LVII), obtained from the chiral amides of carboxylic α-isocyano-acids (LVIII), also gives rise to high values of p when the alkylating agents are benzyl halides, but the yield falls sharply (to 17–35%) when alkyl halides are employed:[116]



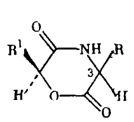
(LVII)



(LIX)

As in the alkylation of dihydropyrazine anions, the diastereoselectivity of the process is probably determined in this instance by the more favourable transition state of type (LIX).[116] The degree of asymmetric induction can be lower in this case than for the anion (LII), since the chiral centre is located further from the reaction centre and the difference between the two diastereoisomers of compound (LVII), in which the metal ion is located above and below the plane of the anion (there is a difference in the interaction of the metal with the Me and R groups), is smaller than in the case of the anion (LII) (the difference between the group R and the atom H).

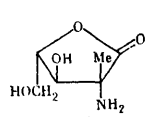
The conversion of 2-furyl- or phenyl-glycines by condensation with hydroxyacids to the corresponding 3,6-dihydro-2*H*-1,4-oxazine-2,5-diones (LX), which react diastereoselectively with R^2X via the C(3) atom, also does not differ fundamentally from the methods considered above:[117,118]



(LX)

R = Ph, 2-furyl

R¹ = $CHMe_2$, CMe_3



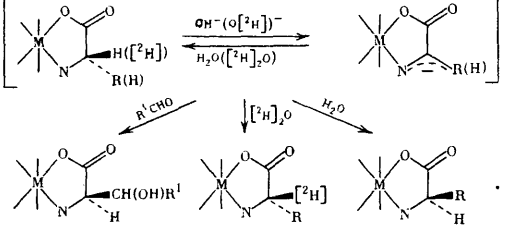
(LXI)

In view of its laborious nature, the method can be usefully employed only in the synthesis of exotic AA (see, for example, Weihrauch and Liebfritz[112]). Thus, the condensation of cyclo-[(*S*)-Ala-(*S*)-Ala] with L-glyceraldehyde yielded the biologically active lactone (LXI).[120] The use of chiral complexes of the Schiff bases derived from AA, examined in the previous Section, is more promising for the synthesis of substituted optically active AA. Interesting results may be expected also in the alkylation of the AA Schiff bases under interfacial conditions in the presence of chiral catalysts, since it is known that the alkylation of racemic phenylindanols with MeI in the presence of *N*-(*p*-trifluoromethylbenzyl)-quinine bromide gives rise to a product with p = 90%.[121]

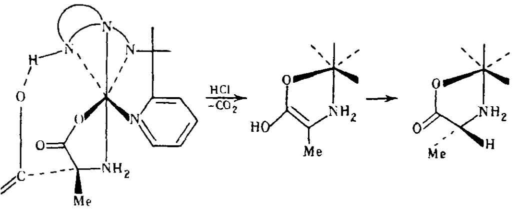
VI. SYNTHESIS AND REACTIONS OF AMINOACIDS VIA TRANSITION METAL COMPLEXES

The ligand in the chiral complexes of transition metals has a rigid orientation and X-ray diffraction analysis provides reliable information about their structure.[122] The intraligand interactions, responsible for the enantioselectivity in these systems, can therefore be assessed very accurately, which facilitates the search for useful synthetic reagents based on them. The stereochemically inert cobalt(III) complexes with amine chiral ligands and aminoacids[123,124] have been used for such purposes for years, for example the cleavage of AA.[125] The chiral recognition of the enantiomers and chiral groups in such complexes occurs mainly as a result of the sterically preferred interaction of one chiral ligand with another or with the prochiral groups of a neighbouring ligand.[126] The introduction into the complex of bonding interligand interactions, which occur for polydentate ligands, enhances the possibility of the chiral recognition of AA.[123,124] The use of chiral derivatives of amines as tetradentate ligands leads to diastereoisomeric Λ and Δ complexes of cobalt(III) with aminoacids, their ratio corresponding to the ratio of the pure AA enantiomers.[127] The epimerisation of the CH aminoacid fragment in the Λ and Δ complexes is catalysed by OH^- (Scheme 4):

Scheme 4



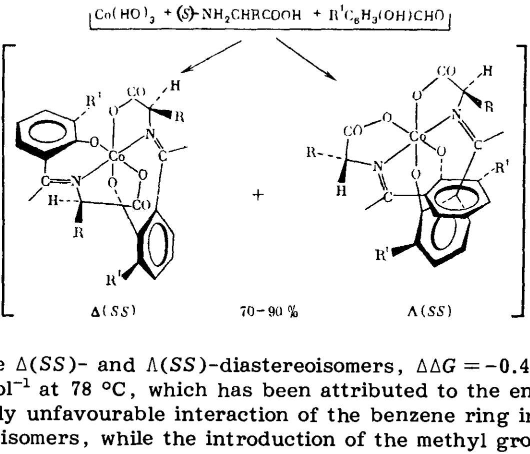
The diastereoselectivity is sometimes high and reaches $\Delta,R/\Delta,S = 91:1$ for the complexes with Asp.[128] Treatment of the racemic α-dichlorotriethylenetetraminecobalt(III) chloride with (*S*)-Pro and Et_3N in boiling alcohol results in 94.5% of the cobalt(III) complex, existing as the Δ complex.[129] Analogous complexes with α-amino-α-methylmalonic acid are used for the acid-catalysed asymmetric carboxylation to Ala.[129] The racemisation of the AA fragment in the isolation stage usually diminishes p,[130] but, for the chiral complexes with (6*R*,8*R*)-6,8-dimethyl-2,5,9,12-tetra-azatridecane[131] and *NN*-di(2-picolinyl)-(1*R*,2*R*)-diaminocyclohexanone,[132] the value of p corresponding to (*R*)-Ala is 66 and 78% respectively. According to Goodwin et al.,[132] the decarboxylation of the cobalt(III) pro-(*S*)-aminomethylmalonate complex affords the (*R*)-alanine complex, i.e. the α-carbon atom undergoes inversion. The mechanism involves the cyclic intermediate (LXIII):



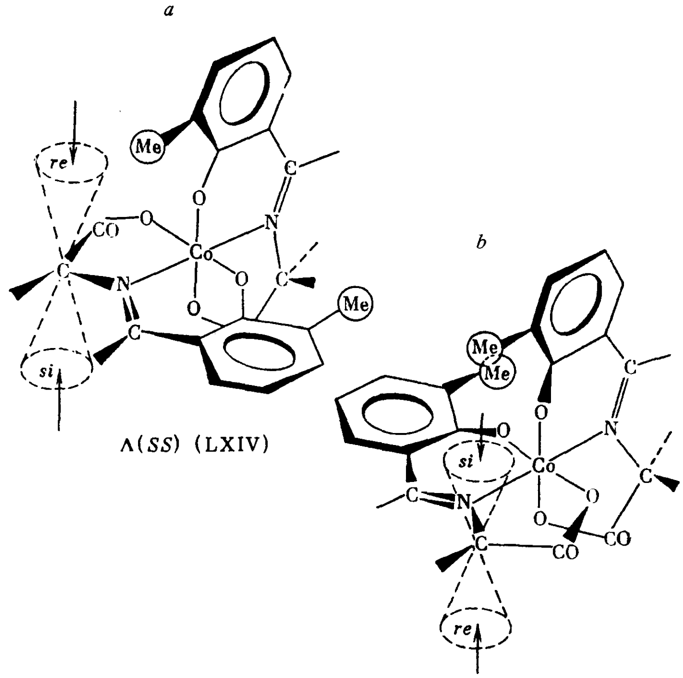
(LXII) (LXIII)

Taking into account the data in Section IV, it has been suggested that the asymmetric induction in compound (LXIII) is effected by the selective intramolecular proton transfer to the enolate fragment from the protonated pyridinium fragment in a chiral environment. The asymmetric decarboxylation of the Λ- or Δ-tetramine complex of cobalt(III) with pyrrolidine-2,2-dicarboxylic acid gives rise to (*S*)-Pro and (*R*)-Pro with p = 20 and 24% respectively.[133] Asymmetric transformations of the AA fragment are possible also in the chiral complexes of dicarbonyl(η^5-cyclopentadienyl) derivatives of molybdenum and tungsten with AA.[134] These complexes are configurationally stable in a neutral solution, while in an alkaline medium rapid interconversion of the diastereoisomers is attained. The epimerisation of the AA fragment suggested[135] and led to the development[136] of the method of synthesis of chiral [^{2}H]Gly and other [2-^{2}H]AA by the enantioselective substitution of the α-proton of the AA by deuterium. It consists in the formation of ethylenediaminecobalt(III) complexes with (*S*)-AA, the separation of the diastereoisomeric complexes by chromatography, deuterium exchange by treatment with OD^- in D_2O, repeated separation of the Δ,S and Δ,R or Λ,S and Λ,R diastereoisomers, and the isolation of AA from the complexes by reduction with $NaBH_4$.[131] The chiral complexes of transition metals have also been used for the asymmetric synthesis of Thr from Gly and MeCHO in 26–33% yield and with p = 16–35% [137] (Scheme 4). The use of simple AA complexes of transition metals suffers from a number of disadvantages, for example, the α-amino-group of the ligand is subjected to electrophilic attack, which prevents the effective synthesis of α-substituted AA by alkylation with alkyl halides.[137] There are also difficulties in selecting the chiral ligands, since the interactions within the complex are readily smoothed out;[126] finally the CH acidity of the complexes is low.[138]

The use of chiral complexes of Schiff bases derived from AA for the synthesis of biomimetic reagents for asymmetric synthesis of AA is more successful. In these complexes, where the kinetic CH acidity of the AA fragment is high,[139] the α-amino-group is reliably protected and the polydentate ligand (the Schiff base) forms a harder complex than the free AA. The relevant studies were carried out initially mainly with stereochemically inert octahedral cobalt(III) complexes, which retain their configuration in the chemical reactions of the ligands.[127,128] The AA Schiff bases with aldehydes form planar tridentate ligands, which can be arranged perpendicularly to one another in the octahedral complexes. The complexes with Gly can be resolved into the enantiomers, while those with other AA can be resolved into diastereoisomers, for example, Λ(*SS*) and Δ(*SS*).[140]



For the Δ(*SS*)- and Λ(*SS*)-diastereoisomers, $\Delta\Delta G = -0.45-1.32$ kcal mol^{-1} at 78 °C, which has been attributed to the energetically unfavourable interaction of the benzene ring in the Λ(*SS*)-isomers, while the introduction of the methyl group in the 3-position in salicylaldehyde (SAL) inverts the stereoselectivity owing to the interaction of the alkyl groups of the AA fragment and the 3-methyl group in the Δ(*SS*)-complexes, which is almost absent in the Λ(*SS*)-isomers.[140] These results make it possible to achieve the synthesis of the partly enriched (*R*)-[^{2}H]Gly and (*S*)-[^{2}H]Gly [147] by analogy with the study of Keges and Legg.[136] The steric shielding of the *re*- and *si*-sides of the intermediate planar carbanion in the complexes Λ-(LXIV) (*re*-side) and Δ-(LXV) (*si*-side) with 3-Me-SAL, which hinders the attack on the pro-(*R*)-proton in the Λ-complexes and the pro-(*S*)-proton in the Δ-complexes and leads to different rates of their exchange with the ratio of the constants up to 1 : 10 (Fig.6), has also been used. Therefore, after the exchange of 50% of the hydrogen for deuterium, (*S*)-[^{2}H]Gly was isolated from the Λ-complex and (*R*)-[^{2}H]Gly was isolated from the Δ-complex with p = 20–40% [141] without the preliminary separation of the diastereoisomers, as in the study of Keges and Legg.[136] The employment of such separation made it possible to obtain the following deuteriated AA with high values of p: (*R*)-Tyr 68%, (*S*)-Tyr (94%), (*R*)-Val (96%), (*S*)-Val)98.8%), (*R*)-NVa (93.4%), (*S*)-NVa (94%), (*R*)-Met (82%), (*S*)-Met (90%), and (*R*)-Ala (90%).[141] The stereochemistry of the formation of the C–C bond obeys the same rule as that for the formation of the C–H bond, but ultimately the thermodynamically stable complex predominates in the final mixture obtained in the condensation with aldehyde. Thus (*S*)-Thr with p = 60% and (*R*)-Thr with p = 73% have been obtained by the reaction with acetaldehyde.[139,140] The interaction with methyl acrylate in H_2O at pH 11.4 afforded a mixture of complexes, after the decomposition of which (*S*)-Gly (p = 10–46%) was isolated quantitatively.[142] Thus both the kinetic acidity of the AA fragment and the enantioselectivity of the formation of the C–C and C–H bonds can be appreciably increased with the aid of chiral cobalt(III) complexes based on the Schiff bases derived from SAL and AA. The use of menthol derivatives as the carbonyl components of the Schiff bases permitted the asymmetric transformation of the AA fragment in the complexes with racemic AA with p = 22% *S* for Ala, 12.6% *S* for Val, and 11.4% *S* for Leu.[143]

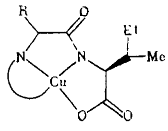


Λ(*SS*) (LXIV)

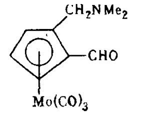
Δ(*SS*) (LXV)

Figure 6. Steric shielding of the *re*- and *si*-sides of the carbanion formed as an intermediate in the Δ(*SS*)- and Λ(*SS*)-complexes of cobalt(III).[141]

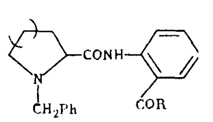
The asymmetric induction in the complexes considered was achieved as a result of the chiral disposition of the ligands within the structure of the complex, which is inert as regards substitution, but effective biomimetic reagents and catalysts[142] must be based on stereochemically labile complexes, capable of ready exchange of the ligands, which inevitably leads to the racemisation at the metal atom. In order to retain the asymmetry of such a labile system, SAL must be replaced by a chiral analogue permitting the use of Ni^{2+}, Cu^{2+}, and possibly Zn^{2+} for the asymmetric synthesis of AA. The use of optically active peptides permitted only the epimerisation of the *N*-terminal AA of the dipeptide in the copper(II) complexes (LXVI):



(LXVI)



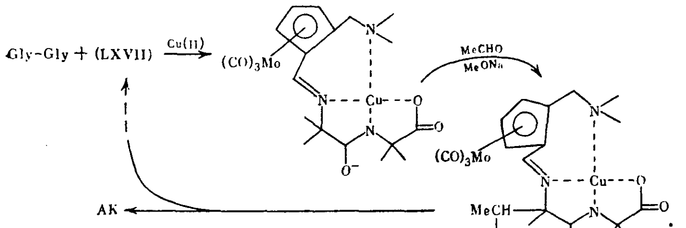
(LXVII)



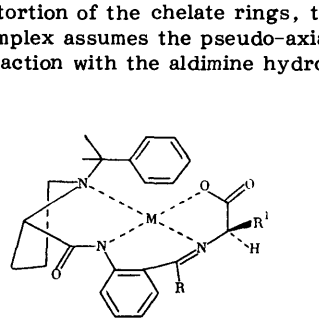
(LXVIII), n = 1, 2
R = H, Me, Ph

Dipeptides with p = 63% *S* for R = Me and 66% *S* for R = Ph have been isolated.[145] The enantiomers of 1-(*NN*-dimethylaminomethyl)-2-formylcymantrene (LXVII) [146,147] have been used as chiral reagents, capable of being regenerated, for the asymmetric synthesis and transformations of AA. Thus the interaction of (+)-(LXVII) with racemic Ala-NVa in the presence of Cu^{2+} and MeONa gives rise to a mixture of diastereoisomers whose ratio shifts towards the most favourable diastereoisomer with (*S*)-Ala (p = 55%) as a consequence of the mobility of the α-proton of the *N*-terminal AA. (*S*)-Thr (p = 92–98%) and (*S*)-allo-Thr (p = 95–100%) were isolated in proportions of 2.15–2.42 and in high yields (after the hydrolysis of the dipeptides) by condensing acetaldehyde with the complex obtained from compound (LXVII), Gly-Gly, and Cu(II):

Scheme 5



(*R*)-Thr (p = 93–96%) and (*R*)-allo-Thr (p = 100%) were obtained in proportions of 2,3 in the case of (–)-(LXVII) [146] (Scheme 5). The greater stability of the complex with (*S*)-Thr can be explained by the fact that, as a consequence of the marked distortion of the chelate rings, the alkyl substituent in the complex assumes the pseudo-axial position, in which the interaction with the aldimine hydrogen is minimal.



(*S*,*R*)-diastereoisomer (LXIX)
R = H, Me, Ph; R^1 = alkyl
M = Ni, Cu

The use of the chiral reagents (LXVIII), having a greater number of coordination sites compared with compound (LXVII), makes it possible to achieve asymmetric transformations also with AA.[29–30,148,149] In the copper(II) and nickel(II) complexes of type (LXIX), obtained in 80–90% yields from the AA and the reagent (LXVIII) in alcohol, the distortions caused by the presence of the asymmetric carbon atom are transmitted to the chelate ring, which entails different interactions of the alkyl residue of the AA and other groups in the complex.[31] These distortions, which are clearly seen in the crystalline state, are retained in solution according to spectroscopic data.[29,31]

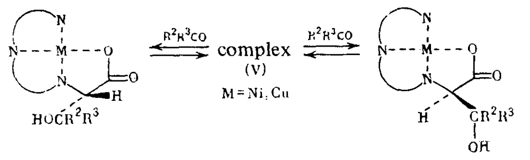
The use of such hard systems makes it possible to alter the enantioselective effects by introducing substituents R in compound (LXIX), i.e. one can alter the ratio of the diastereoisomeric complexes under equilibrium conditions. According to Belokon et al.,[31] this ratio is determined by the difference between the energies of orientation of the alkyl group of the AA towards the benzyl group (upwards from the coordination plane) for the (*S*,*R*)-diastereoisomer (LXIX) or towards the proline fragment for the (*S*,*S*)-diastereoisomer. Non-bonding interactions of the alkyl substituent with the benzyl group, shielding the apical position, are observed in the complex (LXIX), and the increase of the bulk of the group R^1 therefore diminishes the content of the complex with (*R*)-AA. The increase of the bulk of R on passing from H to Me leads to additional distortion of the metallocycles and the assumption of the pseudoaxial position by the alkyl group of the AA. Under these conditions, there is an additional increase of the excess of the complex with (*S*)-AA. The occurrence of large diastereoselective effects in the copper(II) complexes[29] and especially in the nickel(II) complexes,[30,31] reaching p = 90% for the complex with (*S*)-Val, made it possible to achieve the retroracemisation of a series of AA [29–31,150] (Table 5).

Table 5. The enantiomeric composition of the AA after the retroracemisation of the complex (LXIX) [0.2 *N* MeONa, 40° (A); 0.1 *N* MeONa, 25° (B)].

R in (V)	AA	*p*, % for (*S*)-AA		Conditions	Refs.
		Ni (II)	Cu (II)		
H	Ala	15	0	A	[29, 30]
H	Ala	15	0	B*	[31]
H	Phe	40	42	A	[29, 30]
H	Trp	64	—	A	[30]
H	Val	78	54	A	[29, 30]
H	Val	78.5	60	B	[31]
H	NVa	42	12	A	[29, 30]
Me	Ala	82	30	B*	[31]
Me	Val	76	38	B**	[31]
Me	AdAla ***	52	—	B	[31]

*0.012 *N* MeONa. **0.33 *NN* MeONa. ***AdAla = adamantylalanine.

The retention of the characteristic features of the diastereoselective effects also on formation of the C–C bond made it possible to develop a general method of diastereoselective and enantioselective synthesis of β-hydroxy-α-AA by condensing aldehydes or ketones with the nickel(II) and copper(II) complexes of glycine,[151–153] leading to the complexes (LXX) and (LXXI) (Table 6). According to Belokon' et al.,[151] the condensation of compound (V, R = Ph, R^1 = H) with aldehydes under equilibrium conditions leads to the preferential formation of the product (LXX) with the AA side chain directed away from the benzyl group and with the O atom located under the metal atom, which ensures an even greater preference for the (*S*,*S*)-diastereoisomer:

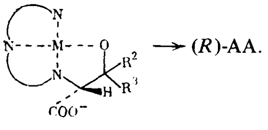


(LXX) (LXXI)

Table 6. Condensation of the glycine complex (V) with carbonyl compounds.[151]

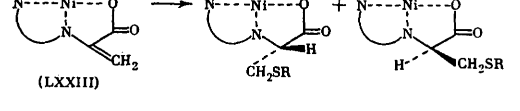
R	M	$R^2R^3C{=}O$	Base	Yield of AA, %	*threo*:*allo*	*p*, %	Configuration
Me	Ni	CH_2O	Et_3N	75–82	—	96	*S*
Me	Ni	CH_2O	MeONa	66–67	—	87–89	*R*
Ph	Ni	CH_2O	Et_3N	75	—	83	*S*
Ph	Ni	CH_2O	MeONa	95	—	88	*R*
Ph	Ni	MeCHO	MeONa	72	20:1	84	*R*
Ph	Ni	MeCHO	Et_3N	32	2:1	78	*S*
Ph	Ni	Me_2CO	MeONa	54	—	72	*R*
Ph	Ni	Me_2CO	MeONa	56	—	98	*R*
Me	Cu	Me_2CO	MeONa	55	—	70	*R*
Me	Cu	PhCHO	MeONa	67	50:1	74	*R*
Me	Ni	PhCHO	MeONa	67	34:1	82	*R*
Ph	Ni	PhCHO	MeONa	67	34:1	82	*R*
Ph	Cu	PhCHO	MeONa	59	50:1	80	*R*

The observed high value p = 95% for the diastereoisomer with (*S*)-Ser (LXX, R^2 = R = H) at low pH is in full agreement with theoretical ideas. At a high pH of the solution, only the (*S*,*R*)-diastereoisomer (LXXII) is formed, which is associated with the ionisation of the hydroxy-group in compounds (LXXI) and (LXXII) and the rearrangement of the complex with coordination of the metal to the ionised hydroxy-group:



(LXXII)

It is noteworthy that, owing to steric hindrance, the second CH_2O molecule does not add to the complex with formation of α-hydroxymethylserine—the main product in the earlier attempts to synthesis Ser from Gly.[154] The preferential formation of the *threo*-products for other aldehydes is also associated with the ionisation of the hydroxy-group at a high pH and the rearrangement of the complexes.[151] The complexes (LXX) and (LXXI) have been converted by acetylation and the elimination of AcOH into the dehydroalanine complex (LXXIII),[155] which combines with thiophenol and phenylmethanethiol via the double bond with formation of the diastereoisomeric complexes of L- and D-*S*-phenyl- or L- and D-*S*-benzyl-cysteines:



(LXXIII)

Chromatographic separation on silica after decomposition yields the enantiomerically pure L- and D-*S*-phenyl- or L- and D-*S*-benzyl-cysteines in an overall yield of 80%.[156,157] The thermodynamic CH acidity of the complexes (LXIX) reaches high values [pK_a = 19.5 (R = R^1 = H), 19.2 (R = H, R = Me), 21.2 (R = H, R^1 = $CHMe_2$), and 18.8 (R = Ph, R^1 = H) in DMSO [158]] and is comparable to the acidity of malonic ester. The high CH acidity of the complexes and their stability have been used to carry out reactions with weak electrophiles—alkyl halides, which made it possible to obtain a series of optically pure α-Me-α-AA for both the (*S*)- and the (*R*)-series[159] (Table 7):

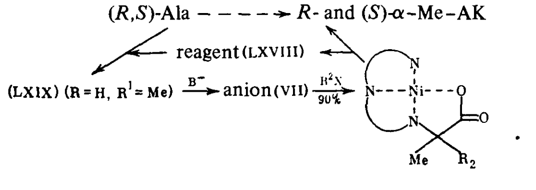


Table 7. The yields of the products of the alkylation of the complex (LXIX, R = H, R^1 = Me) by alkyl halides.[159]

R^2X	BuLi, THF	10% NaOH, CH_2Cl_2
	(*S*, *S*); (*S*, *R*)	(*S*, *S*); (*S*, *R*)
MeI	92	
$PhCH_2Br$	51; 40	63; 31
$CH_2=CHCH_2Br$	56; 33	62; 22

In contrast to the known methods for the alkylation of chiral enolates,[74-79] in this case the deprotonation can be achieved not only with BuLi in THF but also with aqueous alkali under the conditions of phase-transfer catalysis. The separation of the complexes on silica yielded, after decomposition, the optically pure α-Me-AA. Under the conditions of kinetic control, the alkylation of the complex (LXIX, R = R^1 = H) by alkyl halides proceeds with a low value of *p*, which indicates a small difference between the rates of attack by the electrophile on the anion from different sides of the coordination plane. Attack from below, the side opposite to that of the benzyl group, leading to the (*S*,*S*)-diastereoisomer, is somehwat preferable.[159] The use of complexes containing the phenyl group (R = Ph), which imparts the pseudo-axial conformation to the pro-(*S*)-proton, facilitates the attack from below with formation of the (*S*)-AA fragment and increases *p* to 90%.[160]

The general method of asymmetric synthesis of AA via transition metal complexes has many advantages over other procedures. These are the ease of formation of the chiral complexes, mild conditions of the reactions with electrophiles, the high value of *p* for AA, and the virtually complete regeneration of the chiral reagent.

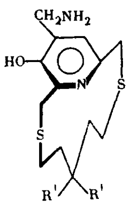
VII. CATALYTIC ASYMMETRIC TRANSAMINATION

The biomimetic approach to the synthesis of a simplified model of enzymic transamination[161] has been applied in a study[162] where the chiral pyridoxamine (LXXIV) with an *ansa*-chain in the molecule, capable of effecting the transamination of α-ketoacids to give AA with *p* up to 9.4% on catalysis by Zn^{2+}, was obtained:

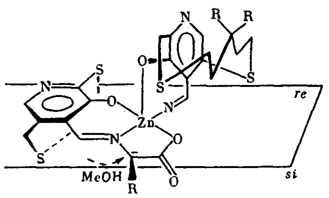
$$RCOCOOH \xrightarrow[Zn^{+2},\ pH\ 4,\ MeOH]{(LXXIV)} AA$$

R	Yield, %	*p*, %	AA	Configuration of (LXXIV)
Me	72	69	*S*-Ala	*R*
$PhCH_2$	60	61	*S*-Phe	*R*
Me_2CH	57	79	*S*-Val	*R*
Me_2CHCH_2	68	96	*S*-Leu	*R*
Me_2CHCH_2	66	94	*R*-Leu	*S*
3-Indolyl	62	60	*R*-Trp	*S*

In the case of MeO[^{2}H], α-deuteriated AA with *p* = 40–90% are isolated:[163]

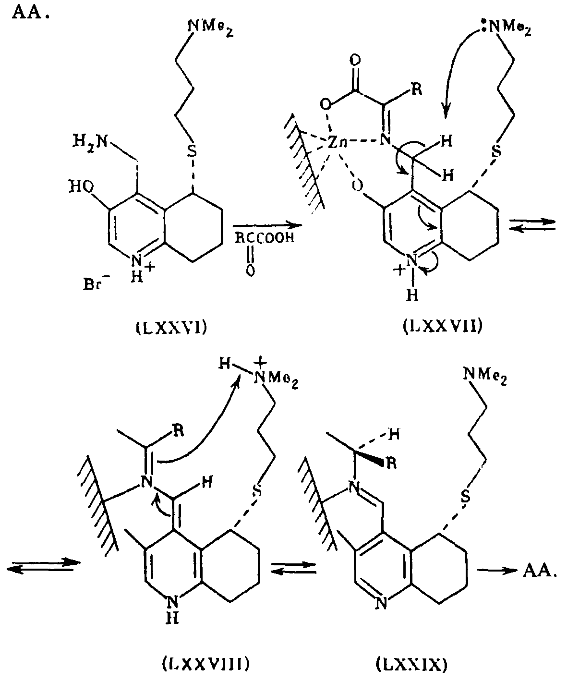


(*S*)-(LXXIV)
R' = H, Me



(LXXV)

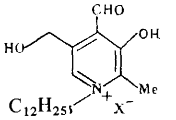
The asymmetric induction can be explained by the kinetically controlled stereoselective protonation of the carbanion formed in the intermediate Zn^{2+} Λ-complex (LXXV). Best results have been obtained with the model (LXXVI), whose activity is even closer to that of an enzyme containing the ε-amino-group in a chiral environment[164]—an analogue of the ε-amino-group of lysine in the active centre of pyridoxal.[161] The dimethylamino-group in the complex (LXXVII) acts as a base for the removal of the pro-(*S*)-hydrogen from 4'-methylketimine, after which the dimethylammonium group approaches, as a consequence of the chiral structure of the complex, the same side of the intermediate (LXXVIII) and, acting as an acid, protonates the α-position from the *si*-side, giving rise to the chiral aldimine (LXXIX) with subsequent liberation of the AA.



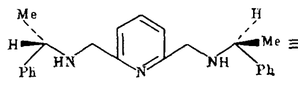
(LXXVI) (LXXVII)

(LXXVIII) (LXXIX)

The following (*R*)-AA were obtained: Ala (yield 83%, *p* =86%), NVa (68%, *p* = 92%), and Trp (89%, *p* = 88%). The use of compound (LXXVI) accelerates the reaction by an order of magnitude owing to the intermolecular general acid—base catalysis compared with the analogue without the NMe_2 group, which a 75% yield of NVa with *p* = 16%. Thus the chiral aldimine can be obtained in two ways—by introducing a steric hindrance through the attack by the carbanion from one side[163] or by the stereoselective protonation of the carbanion.[164] The feasibility of the method is associated with the availability of α-ketoacids and the necessity to employ a metal. The possibility of transamination also without a metal using the achiral *N*-laurylpyridoxal (LXXX) in a cationic micelle under conditions close to physiological conditions has been recently demonstrated.[165] The pyridoxal catalysis has been induced by means of a laser (3371 Å), which also leads to transamination in the absence of enzymes:[166]

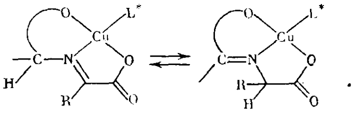


(LXXX)



(LXXXI) .

Another approach is associated with the use of metal complexes of Schiff bases obtained from pyridoxamine and the ketoacid containing compound (LXXXI) as a chiral ligand; a diastereoselective conversion of a ketimine into an aldimine then takes place in the complex.[167] When an (*S*)-ligand is used, the values of *p* for (*S*)-Ala, (*S*)-Val, and (*S*)-Leu are respectively 54, 29, and 48%:

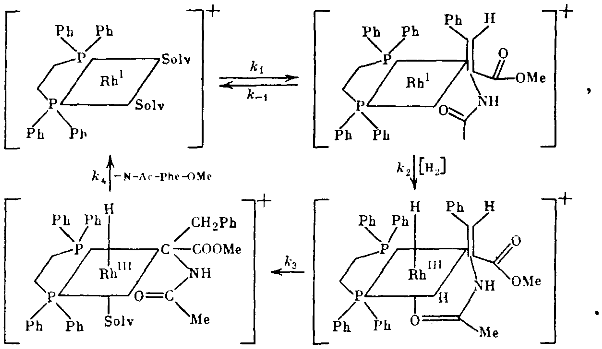


VIII. CATALYTIC ASYMMETRIC REDUCTION

The most effective way of using chiral compounds in the asymmetric synthesis of AA involves their application as catalysts.[168] Striking results have been achieved primarily in the asymmetric reduction of derivatives of prochiral αβ-dehydro-AA (Δ-AA) to the corresponding optically active AA using neutral or, more often, cationic rhodium complexes, containing chiral phosphine ligands, as catalysts.[169] In the reduction of derivatives of α-*N*-acylaminocinnamic acid (AACA), the value of p for many chiral phosphines is close to 100%.[170,171] The results have been described in a series of reviews[28,172–177] and monographs.[178,179] We shall examine data for the determination of the reaction mechanism, the present trends, and the prospects for the method.

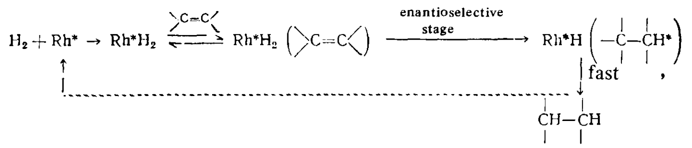
The best rhodium-based catalysts exhibit not only a high enantioselectivity but also a high activity, which approaches that of enzymes and therefore the determination of the mechanism of the reduction of AACA on the basis of the ideas of organometallic and coordination chemistry of rhodium complexes helps also in understanding the effective chiral recognition in such systems. Scheme 6 presents the mechanism of the rhodium complex-catalysed reduction of the AACA ester by Halpern's method.[28] The structure of intermediates was established by spectroscopic methods, resorting in a number of instances to X-ray diffraction;[180–183] the kinetic parameters of all the stages of the catalytic cycle have been determined.[28]

Scheme 6



In the first stage, the formation of a complex with the substrate and the ligand proceeds fairly rapidly and is almost complete even at a low substrate concentration. At 20 °C the second stage of the catalytic cycle—the oxidative addition of hydrogen to the complex—is rate determining and gives rise to a hydride complex in the form of a mixture of the two diastereoisomers (III) and (IV) (Fig.1), characterised at low temperatures as the product of the next stage—reductive elimination.[28] Examination of the structure of the principal diastereoisomer (II) [(II)/(I) > 10 : 1] in solution and in the crystalline state showed that the *re*-side of the substrate is coordinated to rhodium and that the *endo*-addition of hydrogen should give rise to the (*S*)-product, whereas the reaction leads to the isolation of the (*R*)-product with *p* > 95%.[28] It has been shown that the preferential formation of the (*R*)-product is determined by the much higher reactivity of the minor diastereoisomer (I) (Fig.1).[28,184,185]

Ojima and co-workers[186,187] do not dispute this mechanism for the normal reduction conditions but propose an alternative pathway at high hydrogen pressures:

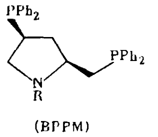


where Rh* is a rhodium complex with a chiral phosphine.

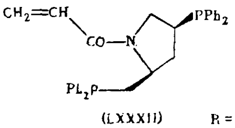
The oxidative addition of H_2 to the complex with the ligand proceeds initially and only then, in the rate-determining stage, does the substrate add on,[186,187] which also agrees with experiment.[188]

One of the important factors influencing the enantioselectivity is the hardness of the complexes (I) and (II) formed. It has been suggested that the lower yields in the reduction of the (*E*)-isomers of AACA compared with the (*Z*)-isomers are associated with the lesser degree of hardness of the complex formed.[186] Effective asymmetric reduction requires the optimum ratio of the rates of the competing reactions in the individual stages of the process, which depends very greatly on the substrate and only AACA or compounds with very similar structures satisfy these requirements.[189] Numerous findings indicating the influence of the form and conformation of the chelate phosphine rings on *p* have demonstrated that five- and seven-membered rings are preferable to six-membered rings owing to the existence of the latter in the rigid chiral C_2-twist conformation.[182,189,190] According to Butler et al.,[183] in a number of instances the size of the chelate ring is of little importance and the principal factor is the nature of the substituent in the phosphine. The main postulate important for the understanding of the stereochemical mechanism of asymmetric hydrogenation has been surveyed by Pavlov and Klabunovskii.[191] It was noted that the stereochemistry of the reaction is determined in the olefin coordination stage with formation of a chelate complex and that the main source of discrimination between the sides of the coordinated prochiral olefin and the catalyst molecule is the chiral disposition of the benzene rings around the phosphorus atom.

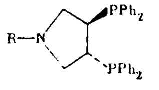
A wide scale search for new and for the modification of the existing phosphine ligands, giving rise to values of *p* close to 100% in asymmetric reduction, has been prosecuted in recent years.[183,192–196] However, the high sensitivity of rhodium catalysts to oxygen and moisture, their high cost, their non-technological nature, and the impossibility of using them at high temperatures, limit their application. There have been only a few successful attempts to reuse a homogeneous rhodium catalyst[197] and also water-soluble diphosphines.[198,199] The problem of the synthesis of chiral organometallic catalysts free from such disadvantages is solved in general by the familiar heterogenisation methods.[200] the synthesis of the rhodium catalyst is usually achieved by introducing a chiral functional group, capable of complex formation, into the achiral matrix. However, the binding of the complexes to mineral clays significantly reduces *p* as a result of the selective absorption of the reduced product by the carrier.[201] Immobilisation on cellulose derivatives gives rise to a low value of *p*,[202] as in the case where a protein is employed as both the carrier and the catalyst.[203] The rhodium complex of BPPM, deposited on charcoal and treated with chromium acetate and Et_3N, gives rise to yields comparable to those of homogeneous reduction (*p* up to 86.5%), which do not fall when the catalyst is reused:[204]



(BPPM)



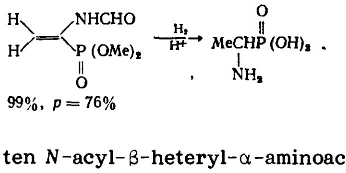
(LXXXII)



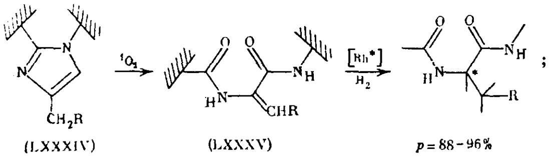
R = H, COPh (LXXXIII)

Best results have been achieved with polymers as carriers.[205,206] Thus optically active phosphine-pyrrolidine monomers (LXXXII) have been obtained, their copolymerisation with hydrophilic monomers and the divinyl monomer affording a cross-linked polymer containing 3–5% of the (LXXXII) fragments, and swelling effectively in the usual hydrogenation solvents.[205] The catalyst was obtained in the usual way by the interaction of $[RhCl(C_2H_4)_2]_2$ with an optically active polymer. Its employment yields *p* = 88–91% for both (*R*)- and (*S*)-N-acylated Phe and DOPA derivatives, the results being equivalent to those obtained under homogeneous reduction conditions. The essential feature of the method consists in a selection of the swellability characteristics of the polymer in the system of solvents employed such that the catalytic section of the polymer is open to interaction with the substrate and is not affected by the functional groups of the main polymer chain.[205] High results have been obtained with (*R*,*R*)-(LXXXIII), synthesised in 8 stages from (*R*,*R*)-tartaric acid with an overall yield of 36%.[207] The rhodium complex of this ligand on the Merrifield resin or SiO_2 permitted the reduction of AACA with *p* = 95% (catalyst/substrate = 1 : 10^4, pressure 50 bar, time h, MeOH). The hydrogenation then proceeds only slightly more slowly than under homogeneous conditions; filtration of the catalyst when the reactions have been completed makes it possible to use it more than once without loss of activity.[207] There is no doubt that the elimination of a whole series of disadvantages of homogeneous rhodium catalysts by their heterogenisation will serve in the future as a stimulus for an even wider employment of these systems. A new approach has been proposed in a study[208] in which the enantioselective hydrogenation of AACA was carried out with the aid of the achiral Wilkinson catalyst—$Rh(PPh_3)_3$—in cholesteryl tridecanoate as a chiral liquid crystal matrix. The temperature dependence of *p* has a maximum corresponding to the middle of the temperature range of the existence of the mesophase. The yield of Phe was 98–100% (*p* = 16%).

Another limitation of rhodium catalysts which prevents their wide scale use in reduction is the small number of substrates which can be used successfully. Thus, satisfactory results have been obtained for eight aminoacids: DOPA, Tyr, Phe, Trp, Ala, Lys, Leu, Val, and some of their derivatives.[171,172,209,210] Their number is now being rapidly expanded. The asymmetric synthesis of the phosphorus analogue of Ala, namely α-aminophosphonic acid, has been carried out over $[Rh\text{-}DIOP]^+$:[21]



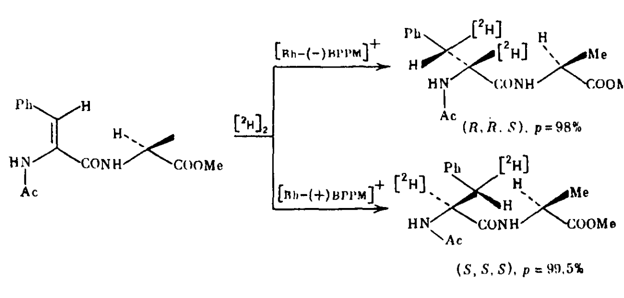
The reduction of ten *N*-acyl-β-heteryl-α-aminoacrylates on this catalyst showed that 2-thienyl, 3-thienyl, 1-methylpyrrolyl, and 3-quinolinyl derivatives are reduced comparatively rapidly with *p* = 20–70%, while the corresponding pyridyl and imidazolyl derivatives are inactive.[212] The photochemical oxidation of cleavage of trisubstituted imidazoles (LXXXIV) with subsequent reduction of the derivatives of Δ-AA amides (LXXXV) has been achieved:[213]



(LXXXIV) (LXXXV) *p* = 88–96%

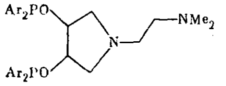
R = H, CHMe₂, Ph .

Overall, the development of the asymmetric reduction stimulated also the develoóment of new ways of synthesising Δ-AA which were previously difficult to obtain.[214] On the other hand, reduction with formation of chiral dipeptides[173,179,197,215] and complex analogues of polypeptides of the type of encephalin[187,216] as well as deuteriated and tritiated polypeptides,[199,217,218] which are difficult to obtain, has also been developing on a wide scale, for example,

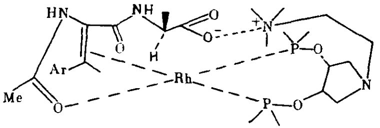


This makes it possible to modify the physiological activity of peptides by inverting the configuration of one or several chiral centres by replacing series of AA by unnatural AA, for example in enkephalin, vasopressin, etc.[187]

The effectiveness of rhodium catalysts in the synthesis of peptides differs somewhat from that for AA.[187] On the other hand, in the reduction of peptides by AACA, ligands forming seven-membered rings produce better results than those forming five-membered rings in view of their greater flexibility, which becomes an important factor when the substrate is polyfunctional.[186] The high enantioselectivity in the reduction of *N*-terminal dehydropeptides (DHP) compared with the *C*-terminal dehydropeptides[219] and also the important role of the *N*-acyl groups, associated with the possibility of their coordination to the Rh atom with formation of a five-membered chelate ring,[218] known also for Δ-AA, has been established. The chiral AA residue in DHP has less influence, since the coordination of its carboxy-group to Rh prevents the oxidative addition of H_2.[218] A detailed study has not been made, but the principal data support the general mechanism proposed for the reduction of AACA [28] (see Scheme 3).



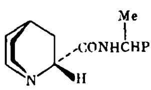
(LXXXVI)



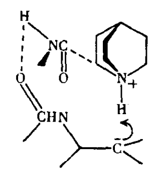
(LXXXVII)

It is of interest that, in the presence of the ω-dimethylamino-group in the ligand (LXXXVI), the diastereoselectivity is inverted also for *N*-Ac-ΔPhe-(*S*)-Phe and the (*S,S*)-dipeptide with $p = 98\%$ is produced.[220] This finding can be explained by the interaction between the NMe_2 group and the COOH group of the peptides, which fixes a definite disposition of the substrate on the catalyst (LXXXVII), while in the case of AACA, where the distance between the groups are large, such interaction does not occur and the yields of (*S*)-Phe are low. The only example of the reduction of bis-DHP over [Rh-DIOP]$^+$ immediately to a mixture of the Phe-Phe dipeptides (*S,S* + *R,R* and *R,S* + *S,R*) is quoted with $p = 9\%$ and 79% respectively.[221] Examples with double asymmetric induction frequently lead to high values of *p*. A stereochemical analysis of such induction within the framework of the interaction of two chiral reagents has been carried out.[173]

The search for effective catalysts using other metals, namely Ru,[222,223] Ir,[224] Pd,[225] and Ni and Co,[226] has been expanded recently. Systems with non-phosphine ligands are promising.[225,227] The development of effective catalysts without platinum group metals is of special interest. A reduction catalysts comprising the complex [Co(dimethylglyoxime)$_2$..base] or [Co(DMG)$_2$.B], used with a chiral catalytic system containing a tertiary amino-group in the α- or β-position relative to the amide group, has been proposed.[227] In the case of $PhCH_2NH_2$ or $P(Ph)_3$ as the base and (*S*)-*N*-[(*R*)-1-phenylethyl]quinuclidine-2-carboxamide (LXXXVII) as the chiral catalyst, the reduction of *NN*-dimethyl-5-benzylidene-hydantoin via compound (LXXXVIII) has been achieved with 93% yield and $p = 79\%$:



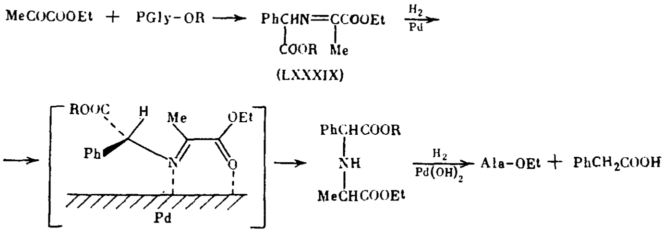
(LXXXVII)



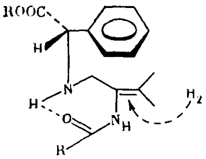
(LXXXVIII)

Thus, the asymmetric protonation of carbanions by chiral acids (Section IV) is a model reaction of the observed catalytic process. The reduction of the AACA ester [in the presence of the chiral catalytic system $CoCl_2$-(+)-neomenthyl-PPh_2-$NaBH_4$] gave $p = 37\%$ for a maximum degree of conversion of 77.5%.[228]

In hydrogenation on heterogeneous catalysts, two procedures are possible—firstly, the use of catalysts modified by treatment with optically active compounds capable of complex formation[229,230] and, secondly, the hydrogenation of the C=C and C=N bonds of the prochiral groups in compounds containing one or more chiral centres. Thus, hydrogenation of derivatives of the AA (LXXXIX) is well known:[231]

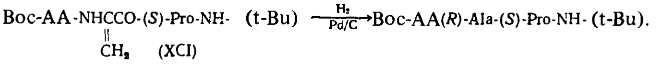


In the latest studies, the AA themselves have been used as the chiral amine,[232] but the values of *p* do not exceed 72% for a yield of 58%. The inadequate rigidity of the binding of the substrate to the catalyst, demonstrated by studying the influence of the solvent and temperature on transamination in compound (LXXXIX),[232] limits the application of the method. Indeed, for the more rigid cyclic systems, for example, in the reductive amination of 2-(*R*)-methylcyclohexanones over Raney nickel, *p* increases to 92–98%.[233] The reduction of acyclic chiral AA amides[234] or DHP [235] proceeds with low values of *p*, while their increase to 40–60% in the case of aromatic compounds can be explained by the formation of structures of type (XC),[235] in which one of the sides of the double bond is shielded and which are analogous to structures (LII)–(LIII), where one of the sides of the chiral carbanion is shielded.



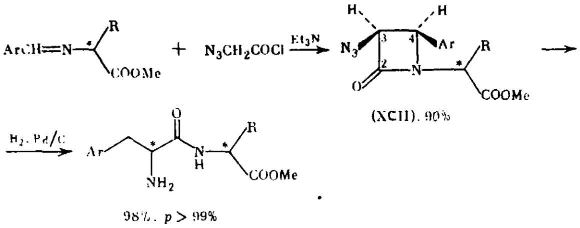
(XC)

The formation of a rigid surface chelate complex has also been proposed in a study[236] where a high value of *p* was obtained in the reduction of linear *N*-Ac-DHP on a nickel catalyst. Indeed the reduction of cyclic DHP on Pd/C usually affords dipeptides with high values of *p* (up to 96–99%).[237] Cyclo-[(*S*)-AA-(*S*)-AA] have been obtained from cyclo-[Δ-AA-(*S*)-AA]; they are hydrolysed to give (*S*)-AA. The reduction of the linear chiral tripeptides (XCI), containing the Δ-AA fragment in the middle unit, has been carried out with $p = 84–93\%$, the use of a C-terminal substituted AA giving better results than the use of N-terminal AA:[238]

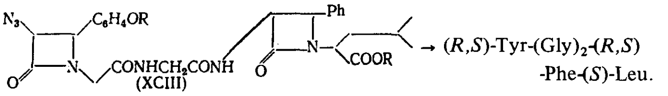


$$\text{Boc-AA-}\underset{\substack{\|\\ CH_2}}{\text{NHCCO}}\text{-(}S\text{)-Pro-NH-(t-Bu)}\ \text{(XCI)} \xrightarrow[\text{Pd/C}]{H_2} \text{Boc-AA(}R\text{)-Ala-(}S\text{)-Pro-NH-(t-Bu).}$$

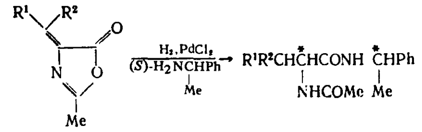
A diastereoselective synthesis of chiral peptides via β-lactams (XCII) has been developed.[239–241] β-Lactams are obtained from the Schiff bases of chiral AA and azidoacetyl chloride and are reduced after the separation of the diastereoisomers (XCII). The essential feature of the method consists in the highly selective cleavage of the N–C(4) bond in the reduction of compound (XCII) on Pd/C:



The use of Schiff bases derived from chiral amines leads to chiral AA amides.[240] The application of β-lactams as chiral synthons[9] made it possible to obtain a series of diastereoisomerically pure oligopeptides, for example a new synthesis of Leu-enkephalin from compound (XCIII) has been achieved:[240]



The reductive ammonolysis of the azlactones (XCIV), for which the rhodium-phosphine catalysts are ineffective, makes it possible to synthesise a wide variety of natural AA.[242] The reduction of compound (XCIV) on $PdCl_2$ with subsequent ammonolysis leads to the corresponding amides N-acetyl-AA:

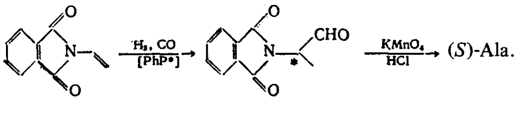


(XCIV)

R^1, R^2=H, Me, $CHMe_2$, Ar .

A yield of 98% with p = 50% (S,S) has been attained for R^1 = 3-MeO-4-$AcOC_6H_3$ and R^2 = H, which made it possible to obtain optically pure (S)-DOPA in 39.5% yield after recrystallisation and hydrolysis.[243]

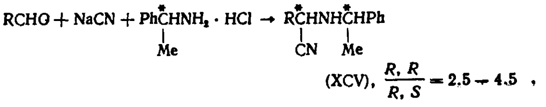
Asymmetric hydroformylation is used little in the synthesis of AA.[244] The N-vinyl derivatives of phthalimides have been converted into (S)-Ala with a yield of 33% (p = 27%)[245] and in a number of instances the yields are even lower:[246]



However, when account is taken of the latest advances in hydroformylation,[168] this application is promising.

IX. THE STRECKER SYNTHESIS

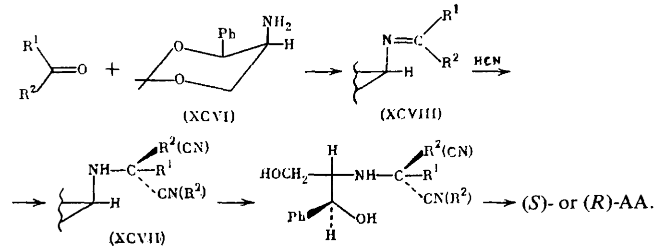
A series of reviews have been devoted to the asymmetric Strecker reaction.[2,3,15] In practice, HCN is usually allowed to react with chiral amines and carbonyl compounds[247] or with the Schiff bases obtained from them beforehand.[248] The recrystallisation of the resulting aminonitriles (XCV) using (R)-$PhCH(Me)NH_2$ makes it possible in a number of instances to raise the yield of the optically active diastereoisomers to 54%.[247] The formation of aminonitriles proceeds subject to thermodynamic control.[15]



$$RCHO + NaCN + Ph\overset{*}{C}H(Me)NH_2\cdot HCl \rightarrow R\overset{*}{C}H(CN)NH\overset{*}{C}H(Me)Ph \quad (XCV), \quad \frac{R,R}{R,S} = 2.5 \rightarrow 4.5\ ,$$

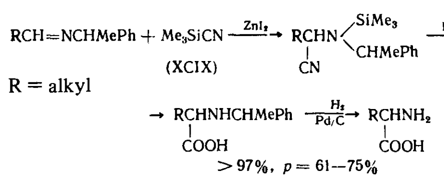
The reaction of acetophenone with HCN and (S)-PhCH(Me).NH_2 results in the preferential formation of the (S,R)-diastereoisomer analogue of compound (XCV), while the (S,S)-diastereoisomer is formed from p-methoxyacetophenone.[249] If the reaction of the readily available (4S,5S)-5-amino-2,2-dimethyl-4-phenyl-1,3-dioxolan (XCVI)[250] with thiophen-2-aldehyde or thiophen-3-aldehyde and HCN is carried out in one stage, (R,S,S)-aminonitriles (XCVII) and respectively (R)-2-thienyl- or (R)-3-thienyl-glycine are formed preferentially, while the intermediate isolation of the imine (XCVIII) results in the preferential formation of the corresponding (S)-AA[248] (Scheme 7):

Scheme 7



Optically pure α-Me-AA,[267] (S)-phenyl- and (S)-anisyl-Gly,[251] (S)-Leu, and (2S,4R)- and (2S,4S)-5,5,5-trifluoro-Leu[252] have also been obtained. The essential feature of the proposed method is the formation of diastereoisomeric readily crystallising aminonitriles (XCVII), whose ratio determines the optical yield of the AA isolated after their decomposition. In a number of instances, only the (S,S,S)-diastereoisomer (with R^1 = CH_2CMe_2OPh and R^2 = Me) or only the (R,S,S)-diastereoisomer (with R^1 = CH_2OPh and R^2 = Me) is formed.[253] In other cases the separation is carried out by recrystallisation.

The Strecker synthesis is nowadays widely used in the multistage method for the preparation of non-protein AA. Pure (S)-γ-carboxy-Glu has been obtained in a low yield from formylmethylmalonic ester in seven stages using (S)-$PhCH(Me)NH_2$.[254] The use of cyanotrimethylsilane (XCIX) is convenient in practice:[255]



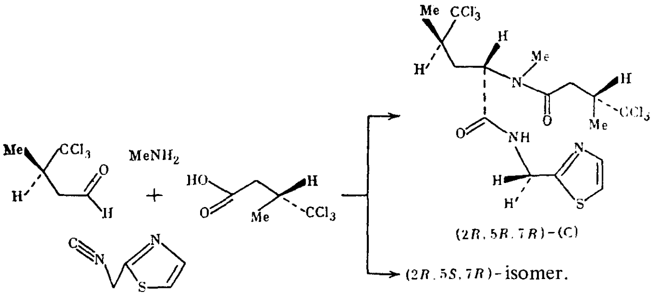
$$RCH{=}NCHMePh + Me_3SiCN \xrightarrow{ZnI_2} RCH(CN)N(SiMe_3)CHMePh \xrightarrow{H^+} (XCV) \xrightarrow{H^+}$$
(XCIX), R = alkyl
$$\rightarrow RCH(COOH)NHCHMePh \xrightarrow[Pd/C]{H_2} RCH(COOH)NH_2\ .$$
$$>97\%,\ p = 61\text{–}75\%$$

The interaction of compound (XCIX) with chiral acetals gives rise to the corresponding cyanohydrins with p = 95%.[256] Thus the Strecker synthesis continues to develop towards the use of new chiral amines in order to eliminate its principal disadvantage—the ready racemisation of diastereoisomeric α-aminonitriles. The use of chiral aminonitriles is being steadily expanded; thus they have been used to synthesise substituted α-hydroxyketones with p up to 97%.[257]

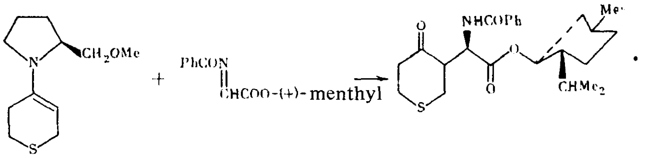
There are great possibilities in the asymmetric catalytic Strecker synthesis. The formation of benzaldehyde (R)-cyanohydrin in the presence of cyclo[(S)-Phe-(S)-His].H_2O takes place with p = 90% for a 40% degree of conversion (PhH, 35 °C, 0.5 h, substrate/catalyst = 1 : 1).[258] The value of p diminishes markedly with increase of the degree of conversion as a result of racemisation.[259] The attempts to carry out the absolute asymmetric synthesis of AA using cyanide compounds, modelling the prebiotic synthesis of AA,[22,260] gave low values of p.

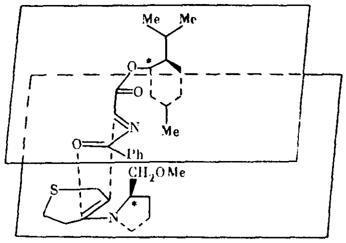
X. OTHER REACTIONS

A successful example of the use of the four-component condensation by the Ugi method is provided by the synthesis of the optically pure peptide (+)-(2*R*,5*R*,7*R*)-13-demethyldysidenin (C) and its (2*R*,5*S*,7*R*)-isomer in 17 and 13% yields respectively:[261]



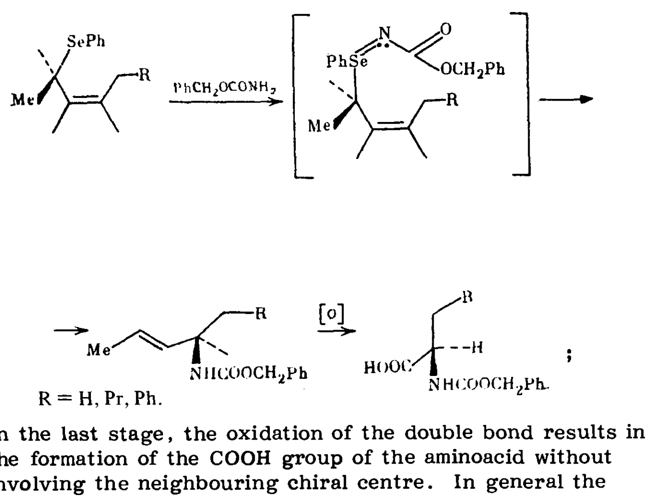
Enantiometrically and diastereoisomerically pure esters of γ-oxo-AA have been obtained[262] via a reaction of the Diels–Alder type, which can be explained by the transition state model (CI)$^{\neq}$.





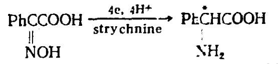
(CI)$^{\neq}$

Here the cooperative effect of the two chiral substituents ensures the stereospecific course of the process and the use of (–)-menthyl ester lowers *p*.[262] The possibility of using the [2,3]sigmatropic rearrangement of substituted optically active selenides for the synthesis of *N*-substituted (*R*)-AA in yields of 58–72% and with $p = 78–84\%$ has been demonstrated:[263]



In the last stage, the oxidation of the double bond results in the formation of the COOH group of the aminoacid without involving the neighbouring chiral centre. In general the oxidation of alcohols and olefins to obtain the carboxy-group is widely used in the synthesis of AA from other optically active compounds: of chiral Gly from D-glucose[264] and of (*R*)-AA from (*S*)-Ser.[23]

Yet another example of the strong influence of the reaction conditions on the optical yield is provided by the electrochemical synthesis of PGly from the oxime of phenylglyoxylic acid in an acetate buffer solution in the presence of strychnine:[265]



$$\underset{\text{NOH}}{\underset{\|}{\text{PhCCOOH}}} \xrightarrow[\text{strychnine}]{4e,\ 4H^+} \underset{\text{NH}_2}{\text{PhCHCOOH}}\ ;$$

cathodic potential, V	–0.95	–1.05	–1.14	–1.30	–1.35
p, %	17.1*R*	11.7*R*	0	10.1*S*	11.1*S*

When a graphite electrode coated with poly-(*S*)-Val is used in this reaction, $p < 2\%$.[266]

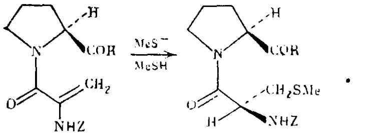
The range of photochemical asymmetric reactions investigated is limited. The first example of asymmetric photolysis, which is especially important for prebiotically valuable substrates such as AA, has been described[267] in relation to the use of (*R*,*S*)-Leu. It has been established that left-(*S*)-circularly polarised light (LCPL), obtained from a laser source with $\lambda = 212.8$ nm, effects the preferential photolysis of (*S*)-Leu, while right-(*R*)-polarised light (RCPL) effects the preferential photolysis of (*R*)-Leu. An enantiomeric excess of 1.98 has been obtained for a 52% degree of conversion with RCPL and of 2.5 for a 75% degree of conversion with LCPL. The stereocontrolled photoalkylation of the Gly residue in the peptide chain proceeds with *p* up to 40%.[268] When the reaction

$$[(S)\text{-Ala-Gly-}(S)\text{-Ala}]_n \xrightarrow[\text{toluene}]{h\nu} [(S)\text{-Ala-}(S)\text{-Phe-}(S)\text{-Ala}]_n \rightarrow (S)\text{-Phe}$$

is carried out in but-1-ene, it is possible to obtain (*R*)-NLe with *p* up to 20%:

$$[(S)\text{-Pro-Gly-}(S)\text{-Pro}]_n \xrightarrow[\text{but-1-ene}]{h\nu} (R)\text{-NLe}.$$

The biomimetic formation of Cys with high chemical) up to 95%) and optical ($p = 85\%$) yields has been achieved:[269]



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Chemical asymmetric synthesis makes it possible to obtain any aminoacids with natural and non-natural structures and configurations in virtually quantitative optical yields. A particular advances has been attained in the use of general methods such as catalytic asymmetric hydrogenation and enantioselective alkylation of carbanions generated from aminoacid derivatives. In a number of instances, high optical yields have been attained with double asymmetric induction when the enantioselectivity of the process is determined by two asymmetry centres already present.

The theory of asymmetric induction has been developed to only a very slight extent, because the small differences between the energies of the diastereoisomeric transition or final states which are sufficient for the attainment of a high enantioselectivity of the synthesis are a consequence of slight steric or electronic requirements, which are as a rule difficult to take into account.

The majority of asymmetric syntheses have not been developed as preparative syntheses of aminoacids—their assessment is frequently based on the NMR or GLC analysis of the reaction mixtures. None of the asymmetric syntheses of aminoacids has so far found a serious industrial application, while the separation of enantiomers by crystallisation is very common. Analysis of the literature shows that this is caused by, on the one hand, the high cost and the difficulty of regenerating chiral rhodium compounds, the most effective catalyst of asymmetric synthesis, and, on the other hand, by the fact that the known chiral reagents for asymmetric synthesis, capable of being regenerated, are not as yet capable of propagating the catalytic process. These deficiencies predetermine the direction of the most promising research. Certain optically active aminoacids have become a readily available and cheap source of chirality. In many methods for asymmetric synthesis, they are used as a basis for the preparation of chiral reagents and catalysts.

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During the preparation of the review for printing, additional data have appeared in literature. In particular, a chiral polymeric rhodium catalyst based on 3,4-(*R*,*R*)-bis-(diphenylphosphino)pyrrolidine has been obtained. When AACA and its methyl ester were reduced in its presence, products with p up to 100% were obtained.[270] The activity of the catalyst falls after repeated use. The possibility of the quantitative isolation of rhodium after the completion of the reaction has been demonstrated.[271] New data concerning the mechanism of asymmetric reduction have been published.[272] The use of a chiral polymeric platinum catalyst based on DIOP derivatives permitted the hydroformylation of *N*-vinylphthalimide with p up to 70%.[273] The asymmetric aldol reaction of aldehydes with isocyanates, catalysed by the chiral ferrocenylphosphine gold(I) complex, leads to AA with a high value of p.[274]

Poly-L-Val (2%) on CdS catalyses the synthesis of Asp from fumaric acid and NH_4Cl on UV irradiation with $p = 60\%$.[275]

A review has been devoted to the biomimetic transamination of α-ketoacids.[276]

The synthesis of AA with $p > 95\%$ from α-halogenosulphonamidoisobornyl ethers has been published.[277]

(*R*)-*N*-substituted AA have been synthesised from (*S*)-hydroxyacids.[278]

A review has been published on the regio-, diastereo, and enantiostereoselective reactions leading to the formation of a C–C bond using metallated derivatives of aminonitriles, etc.[279]

The aldol reaction of a chiral enolate containing the Gly fragment with RCHO made it possible to obtain a series of enantiomerically pure β-hydroxy-*N*-methyl-AA.[280]

The catalytic asymmetric synthesis of chiral AA amides unsubstituted in the α-amino-group from trifluoromethyl derivatives of azlactones has been achieved.[281]

The use of 2-t-butyl-1,3-oxazolin-5-ones for the synthesis of optically pure α-vinyl-,[282] α-alkyl-,[283] and β-hydroxy-AA [284] proved to be more convenient than the use of compound (XLIV), which is their analogue.

In the continuation of studies on the bislactim method of synthesis of AA, the reactions of cyclo[L-Val-Gly] with epoxides ($p > 95\%$) and Michael addition to activated olefins ($p > 95\%$), with subsequent isolation of the corresponding (*R*)-Ser [285] and (*R*)-Glu [286] have been carried out. (*R*)-Pro, [287] cyclic optically pure AA,[288,289] and various non-protein AA [290] have also been obtained. A simple synthesis of α-aminocyclopropanecarboxylic acid has been described.[291]

The use of the general asymmetric method of synthesis of AA via chiral nickel(II) complexes of type (LXIX) made it possible to synthesise enantiomerically and disastereomerically pure β- and γ-substituted Glu and (*S*)-Pro by condensing Gly with activated olefins;[292] the reaction with alkyl halides affords optically pure AA derivatives.[293]

The possibility of the electrophilic asymmetric amination of various chiral enolates, obtained from carboxylic acid derivatives, by di-t-butyl diazodiformate, has been demonstrated simultaneously in a number of studies.[294–297] The optical yield of α-hydrazinoacids and correspondingly the α-aminoacids reached 99%.

The latest reviews on asymmetric synthesis include also data on AA.[298,299]

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Structural Study of Organic Polymers by the Microdiffraction Electron Microscope Method

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The advances achieved by the method of electron microdiffraction in the study of the crystal structures of organic polymers with the aid of the transmission electron microscope are examined and the advantages and disadvantages of the method are analysed. It is shown that the diffraction studies on polymers in a transmission electron microscope not only supplement X-ray data but in many cases provide unique possibilities for structural analysis. The applied aspect of the structural studies of polymers is examined and methods are described for the preparation of the specimens and for protecting the polymeric object from the action of radiation.

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I. INTRODUCTION

Modern electron microscopy (EM) has an enormous potential, providing great possibilities for the study of the microstructures and compositions of substances and materials.[1] The structural motif of the crystal at the level of the detailed atomic structure can be visualised on high-voltage instruments. The method for the recording of electron diffraction in a selected region—electron microdiffraction (EMD), which carries information about the crystal structure, has been brought to a high degree of perfection. The EM results are supplemented by using spectroscopic-analytical devices (analysis of the energy losses by electrons, dispersion of energy, and emission—X-ray, Auger, etc.); all the elements ranging from sodium to uranium can be detected. Electron microscopy has begun to be used in crystal-chemical studies on polymers, which are difficult objects for EM because of their lack of resistance to radiation damage by the electron beam.

When transmission electron microscopy (TEM) is used for the solution of structural problems in polymer chemistry, it has now become possible to achieve in practice simultaneously the recording of the EMD pattern and of the image of the corresponding section of the object under the conditions of light and dark fields. Quantitative analysis of the data makes it possible to determine the structure of the crystalline region of the polymer, including the chain conformation with the coordinates of the atoms and the packing of the macromolecules. When the reflection intensities on the electron diffraction pattern are used, both experimental and computational—theoretical problems arise. As regards the experimental technique, there is the question of the development of standard methods for the preparation of the specimens which do not introduce artefacts into the investigation and which are suitable for obtaining an electron diffraction pattern with a high information content. This includes the problems of protecting the object against radiation damage and of increasing the quality of the EMD pattern, the accuracy of the measurements, etc. Problems of another kind include those of justifying the application of the kinematic approximation to the calculation of the structural diffraction amplitudes, the development of methods for the determination of the chain conformation, etc. These questions are considered in the present review, whose aim is to discuss the possibilities and advances achieved by the EMD method in structural research into organic polymers.

II. THE INFORMATION CONTENT AND VALIDITY OF THE RESULTS OF THE STRUCTURAL STUDY OF POLYMERS BY ELECTRON MICRODIFFRACTION

The theoretical principles of electron diffraction have been described in the monographs of Pinsker,[2] Vainshtein,[3] Cowley,[4] etc. In relation to TEM, the theory and practice of the use of the EMD method have been examined in a series of monographs and manuals by Soviet and foreign authors.[5-12] However, virtually no attention is devoted in these publications to the study of polymers and only Fischer's review,[5] published in 1964, is wholly devoted to this question. Specific data, characterising the contribution of the EMD method to structural research into polymeric compounds by the beginning of the 1980's, have been described in a report to a symposium of the American Chemical Society.[13]

It is noteworthy that, in relation to polymers, the electron diffraction method is relatively new and has developed "in the footsteps" of X-ray diffraction; therefore, in view of the aims of this review, it is useful to consider briefly the general postulates characterising the similarity and differences between electron and X-ray diffraction.

The information content in the electron diffraction pattern is determined primarily by the fact that (as in the case of X-rays) it makes it possible to recreate the molecular and atomic structure of a substance by means of calculations based on the concept of the inverse space of the crystal. In assessing the possibilities of the electron diffraction method, it must be emphasised that the electron microscope has undoubted advantages over the electron diffractometer, making it possible to combine the analysis of the diffraction pattern with the visual study of the microstructure of the corresponding section of the object. This is especially effective in the direct resolution of the crystal lattice.

In the microdiffraction mode of the operation of the transmission electron microscope, one obtains electron diffraction patterns of three main types depending on the phase state of the polymer: ring patterns (from polycrystalline specimens), point or arc patterns (from single crystal specimens), and texture patterns (from axially extended films and fibres).

An electron diffraction pattern of the first type indicates the crystallisation of the polymer and makes it possible to characterise the structure of the crystalline region by a set of interplanar spacings. The electron diffraction pattern of a single crystal consists of one of the planar sections through the inverse lattice; for the complete representation of the inverse lattice in order to determine the geometry of the unit cell, it is necessary to obtain a series of diffraction patterns for different orientations of the specimen relative to the incident beam. A texture electron diffraction pattern with arc reflections along the equator and layer lines is formed when the incident beam is directed at right angles to the extension axis of the specimen and represents either the entire or almost the entire inverse lattice making it possible to calculate the crystallographic parameters and the repeat period of the macromolecule.

The first stage of the microdiffraction study yields structural characteristics such as the space group, the unit cell parameters, the volume and density of the unit cell, the number of monomer units, and the number of chains in the cell. Furthermore, the determination of the intensities of the reflections and calculation of the experimental structural diffraction amplitudes yield information for the determination of the chain conformation and the atomic coordinates and also of the molecular packing by mathematical procedures widely developed previously in relation to X-ray diffraction. The two diffraction methods are similar both as regards the nature of the physical processes and the methodology of the treatment of the experimental data, although they have their advantages and limitations due to the characteristics of the radiation and of the experimental techniques.

X-Rays are scattered by the electron clouds of atoms, while electrons are scattered by the potential generated by the atomic nuclei and their electron clouds. The advantages of electron diffraction are associated primarily with the much shorter wavelength of the electrons, which depends on the accelerating potential:

$$\lambda = h/(2meV)^{1/2} = 12.225/V^{1/2},$$

where h is the Planck constant, m the mass of the electron, V the accelerating potential, and e the electronic charge. The non-relativistic wavelength of the electrons at an accelerating potential of, for example, 100 kV or 1 MV is 0.037 and 0.0087 Å respectively, while the wavelength of X-rays is 1.54 Å (copper anode, K_α line). High-voltage microscopes with accelerating potentials ranging from 500 to 3000 kV have now been developed, which possess a whole series of unique possibilities, in particular they make it possible to raise the resolution on the image (which depends on the wavelength) to the atomic-molecular level.

In connection with the appreciably shorter wavelength, the region of the inverse space of the crystal detected by the EMD method has expanded sharply, on the one hand, and the energy of the interaction of the radiation with the substance has increased, on the other. The characteristic features of the scattering of electrons on passage through the object result in a much greater number of reflections in the diffraction pattern and their intensity is 10^6–10^8 times greater than in the scattering of X-rays. For example, structural analysis by the electron diffraction method makes it possible to determine the positions of the hydrogen atoms, although the ratio of their structural amplitudes to the amplitudes of the carbon atom is much higher than in X-ray diffraction.

Apart from the fundamental advantages indicated above, there are also preparative advantages, namely electron microscopy makes it possible to investigate single microcrystals of the polymer, while the X-ray diffraction method operates mainly with macrospecimens in an oriented crystalline state; therefore the EMD method provides a unique possibility for the structural study of crystalline polymers which are incapable of orientational stretching. When the polymer can be obtained in the form of an oriented crystalline specimen, the possibility of obtaining the electron diffraction pattern of a single crystal together with a texture electron diffraction pattern and a texture X-ray diffraction pattern is also extremely important, since it makes it possible to overcome a series of disadvantages which lower the information content of the experimental data for the texture.[14] The disadvantages of the difraction pattern of the axial texture include the small number of Bragg maxima and the relatively low intensity, which has an especially negative effect on the reflections which require a high resolution; furthermore, a partial loss of reflections is observed owing to their overlap and disappearance against the diffuse scattering background due to the amorphous regions of the specimen.

The electron diffraction patterns of single crystals are free from the above limitations. They exhibit a greater number of reflections in the basal plane and their intensity is higher, which increases the information content of the diffraction data and in particular it makes it possible to refine the character of the systematic extinctions.[13] For example, in the study of poly(trimethylene terephthalate) it was shown[15] that the X-ray diffraction pattern of the fibre has 5–10 equatorial reflections with $hk0$ indices, while the electron diffraction pattern of a single crystal contains at least five times more reflections due to the basal plane, from which the space group and the unit cell parameters were determined acurately.

As regards the comparison of the X-ray and electron diffraction patterns of the axial texture, both methods provide analogous information, although the higher intensity of the reflections on the remote layer lines of the texture electron diffraction pattern makes it possible to determine more accurately the repeat period of the macromolecule.[16] It is noteworthy that the advantages of the texture electron diffraction patterns were elucidated already at an early stage in the development of electron diffraction and were demonstrated in a study[17] of the structure of cellulose.

The disadvantages of the EMD method are caused primarily by the fact that the electron microscope equipment is much more complex than the X-ray diffraction equipment and much more stringent requirements must be met by the technical state of the microscope, the correct focusing of the objective, the quality of the calibration of the apparatus constant, etc. Furthermore, the probability of error increases as a consequence of the effect of radiation on the microspecimen. For example, in the study of the structure of poly(trifluoroethylene) it was established[18] that the damage of the specimen on irradiation leads to unduly high unit cell parameters compared with X-ray diffraction data. The authors of special manuals on practical electron microscopy have arrived at the unambiguous conclusion that the accuracy of measurements based on electron diffraction patterns with the maximum possible prevention of errors is at least to within 0.1% of the measured interplanar spacings. One of the most important factors governing the improvement of accuracy is the calibration of each electron diffraction pattern by the vacuum sputtering of a test object (TlCl, Au, Al) on the electron microscope grid holder.

The fundamental problem of taking into account the dependence of the intensity of the reflections on structural amplitudes arises in structural analysis based on electron diffraction data.[3,4,8] The corresponding calculations in electron diffraction studies are carried out in terms of the so called kinematic theory of the scattering of waves by crystals. This presupposes that, under the influence of the primary beam, each atom becomes a source of secondary spherical waves, whose amplitude is much smaller than the amplitude of the initial wave. The scattering process is not accompanied by a change in wave length and there is no repeated scattering of the waves already scattered or such scattering may be neglected. Being propagated in all directions with phase relations determined by the geometry of the relative positions of the scattering centres, the secondary waves interfere with one another and determine the overall intensity of the reflections. However, since in the absence of X-rays the electrons strongly interact with the substance, the application of the kinematic theory is limited by the conditions stipulating a small thickness of the crystal (100–150 Å) and the absence of its bending on the support. Otherwise the intensity of the diffraction maxima may be influenced by dynamic scattering, i.e. by the repeated scattering of the already scattered electrons.

The two-wave approximation of the dynamic theory presupposes that only two waves—primary and diffracted—interact in the crystal. The multiwave theory takes into account both the multiple interaction of the diffracted waves and the finite size of the object, the different energy losses, etc. The role of dynamic scattering increases if the molecule contains heavy atoms and also with increase in the accelerating potential. Cowley,[19] Goodman and Moodie,[20] as well as Dorset and Moss[21–23] have been concerned with the influence of dynamic scattering on structural diffraction amplitudes. In relation to the analysis of diffraction by thin and deformed crystals of paraffins, the last workers demonstrated that the kinematic theory of scattering can be adopted as a suitable approximation in the calculation of the atomic structure, but in each specific case it is necessary to check the influence of the dynamic scattering in order to complete the investigation and to obtain a reasonable agreement between the experimental and calculated structural amplitudes.

III. ADVANCES AND PROSPECTS IN THE APPLICATION OF THE MICRODIFFRACTION METHOD TO THE DETERMINATION OF THE CRYSTAL STRUCTURES OF ORGANIC POLYMERS

The first studies on polymers by the electron diffraction method were carried out by Soviet workers using an electron diffractometer at the beginning of the 1950's.[24–28] Precision studies involved the determination of the structure of a synthetic polypeptide—poly(γ-methyl-L-glutamate)[29] and the refinement of the atomic coordinates (including hydrogen) in the poly(ethylene terephthalate) macromolecule.[30] There is no doubt that studies at this level prepare the ground, as it were, for the development of quantitative microdiffraction methods.

Systematic studies on organic polymeric compounds by the TEM method began at the end of the 1950's and the possibility of microdiffraction observations was already used in the first classical investigations by Till,[31] Keller,[32] and Fisher.[33] The results obtained by the EMD method played an important role in the development of ideas about the characteristic features of the crystallisation of macromolecules[34–36] and the hypothesis of the folding of polymer chains was put forward on the basis of the electron diffraction patterns of a thin film of guttapercha long before the start of systematic research into the crystallisation of polymers.[37] However, the problem of applying EMD to the structural analysis of polymers was not formulated and solved until 1974 when Claffey et al. demonstrated the possibility of using the reflection intensities in the electron diffraction pattern of a single crystal in a study of poly[3,3-di(chloromethyl)-oxacyclobutane].[38] The authors were able to confirm the X-ray diffraction data for the cell geometry, to refine the space group, and to determine the atomic coordinates and the conformation of the side chains.

The crystal structures of polymers according to electron microdiffraction data.

No.	Polymer	Unit cell parameters	Chain conformation	*R* factor	Refs.
(I)	Poly(*p*-oxyphenylene-*m*-carbaboranyl)	Orthorhombic; $a = 11.40$, $b = 7.70$, $c = 18.0$; $\rho_c = 1.29$, $\rho_a = 1.17$; $z = 4$, $n = 2$	—	—	[39]
(II)	Poly(dipropyl-siloxane)	Tetragonal; $P4_3$, $a = 9.52$, $b = 9.40$; $\rho_c = 1.015$; $z = 4$, $n = 1$	$H(4/1)$	—	[40]
(III)	Poly[diphenyl(phenyl-*p*-tolyl)siloxane]	Orthorhombic; $a = 21.06$, $b = 10.53$, $c = 10.36$; $\rho_c = 1.17$; $z = 8, n = 2$	$H(4/1)$	—	[41]
(IV)	Poly(phenyl-*p*-tolyl-siloxane)	Orthorhombic; $a = 21.0$, $b = 10.86$, $c = 9.97$; $\rho_c = 1.24$; $z = 8, n = 2$	$H(4/1)$	—	[41]
(V)	Poly(vinylidene fluoride), γ-form	Monoclinic; $a = 4.96$ $b = 9.67$, $c = 9.20$; $\gamma = 93°$	$P(T_3GT_3\bar{G})$	—	[42]
(VI)	Poly(bistrifluoro-ethoxyphosphazene)	Monoclinic; $a = 10.03,3$, $b = 9,37$, $c = 4,86$; $\gamma = 91°$	—	—	[43]
(VII)	Poly(bisphenoxyphos-phazene)	Monoclinic; $a = 16.6$, $b = 13,8$, $c = 4,91$; $\gamma = 83°$	—	—	[43]
(VIII)	Poly(*p*-oxybenzoyl)	Orthorhombic; $P2_12_12_1$ or $P222_1$, $a = 7.62$, $b = 5.70$, $c = 12.56$; $\rho_c = 1.46$; $z = 4, n = 2$	$P(2/1)$	—	[44 45]
(IX)	Poly[3,3-*bis*(chloro-methyl)oxacyclo-butane], α-*form*	Orthorhombic; $Pna2_1$; $a = 17.85$, $b = 8.15$, $c = 4.78$; $z = 4$, $n = 4$	$Z(TT)$	0.247; $N = 20$	[38]
(X)	Poly(ethylene sulphide)	Orthorhombic; $a = 8.508$, $b = 4.93$, $c = 6.686$; $z = 4$, $n = 2$	P	0,33; $N = 20$	[14]
(XI)	Cellulose triacetate	Orthorhombic; $P2_12_12_1$, $a = 24.68$, $b = 11.52$, $c = 10,54$; $z = 8$, $n = 4$	$H(2/1)$	0.26; $N = 40$	[48]
(XII)	Poly(trimethylene terephthalate)	Triclinic; $a = 4.637$, $b = 6.266$, $c = 18.64$; $\alpha = 98.4°$, $\beta = 93.0°$, $\gamma = 111.1°$, $\rho_c = 1.138$, $z = 2$, $n = 1$	$P(TGGT)$	0,255; $N = 25$	[15]
(XIII)	Poly(β-oxybutyroyl)	Orthorhombic; $P2_12_12_1$; $a = 5,76$, $b = 13.2$, $c = 5,96$; $z = 2$, $n = 2$	$H(2/1)$	0,33; $N = 28$	[49]
(XIV)	Poly(hexamethylene terephthalate), form I	Triclinic; $P\bar{1}$, $a = 5.217$, $b = 5.284$, $c = 15.738$; $\alpha = 12.94°$, $\beta = 9.76°$, $\gamma = 95.6°$, $z = 1$, $n = 1$	P	0 172; $N = 19$	[13. 50. 51]
(XV)	Poly(hexamethylene terephthalate), form II	Triclinic; $a = 5.217$, $b = 10,568$; $c = 15.738$; $\alpha = 129.4°$, $\beta = 97.6°$, $\gamma = 95°$, $\rho_c = 1.278$; $z = 2$, $n = 2$	P	0.161; $N = 19$ и 0.196; $N = 24$	[50. 51]
(XVI)	Poly(hexamethylene terephthalate), form III	Monoclinic; $a = 9.10$, $b = 17.56$, $c = 15.74$; $\alpha = 127°$; $z = 6$, $n = 6$	P	—	[50 51]
(XVII)	*trans*-Polyacetylene	Orthorhombic; Pna, $a = 7.32$, $b = 4,24$; $c = 15.74$; $\rho_c = 1.13$; $z = 4$, $n = 2$	$Z(2/\bar{1})$	0.24; $N = 23$	[52]
(XVIII)	Poly(*p*-xylylene), β-form	Trigonal; $P3$, $a = 20.53$, $c = 6.55$; $\gamma = 120°$; $\rho_c = 1.58$; $z = 16$, $n = 16$	P	0.21; $N = 25$	[53. 54]
(XIX)	Poly(2,4-*trans*-cyclo-hexanediyldimethyl-ene succinate)	Monoclinic; $P2_1n$, $a = 6.486$, $b = 9.482$, $c = 13.51$; $\beta = 45.9°$; $\rho_c = 1.259$; $z = 2, n = 2$	$P(GGTT)$	0.199; $N = 87$	[55, 56]
(XX)	Poly(dodeca-1,11-diyne) macromonomer	Monoclinic; $P2_1/n$, $a = 13.25$, $b = 14.15$, $c = 7,63$; $\beta = 118.5°$; $z = 2$, $n = 4$	P	0.13; $N = 17$	[57]
(XXI)	Product of solid-phase polymerisation of the macromonomer (XX)	Monoclinic; $P2_1/n$, $a = 9.17$, $b = 12.25$, $c = 9.92$; $z = 4$, $n = 4$	P	0.13; $N = 36$	[57]

Notation: ρ_c is the density of the crystal, ρ_a the density of the amorphous specimen, z the number of units in the unit cell, n the number of chains in the unit cell, N the number of reflections on the electron diffraction pattern; the following notation has been adopted for the chain conformation: H = helix, P = planar, Z = zigzag, T = *trans*, and G = *gauche*.

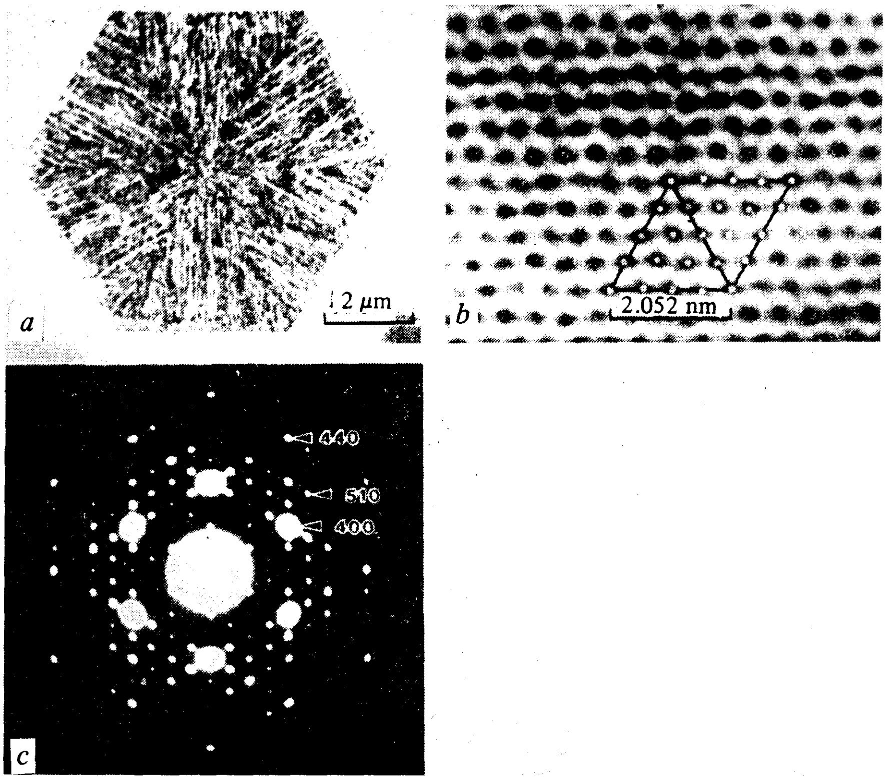

Figure 1. The electron microscope study of poly(*p*-xylene):[53] *a*) single crystal of the β-form; *b*) image of the crystal lattice obtained with the aid of a high-voltage microscope having a resolution of 0.20–0.15 nm; each dark spot corresponds to the projection of the macromolecule onto the basal plane and the white circles indicate the position of the macromolecules in the unit cell; *c*) electron diffraction pattern of a single crystal of the β-form; the numerals denote the indices of the corresponding reflections.

One of the most important results of their study[38] was the demonstration of the applicability of the kinematic approximation to the calculation of structural diffraction amplitudes. This study influenced the general level of electron microscope investigations of polymers and opened up ways to the use of TEM as a method for structural analysis. Since its publication,[38] more than 10 years have elapsed, but one must conclude that the development of research on these lines is relatively slow evidently due to the experimental difficulties in the preparation of the objects and the determination of electron diffraction patterns of a sufficiently high quality and with an adequate information content; the main bulk of the determinations of the structure of polymers are therefore carried out at the present time by the X-ray diffraction method. On the other hand, in recent years there have been undoubted advances in the use of EMD.

The advances achieved with the aid of EMD can be analysed by means of a Table which presents the most accurate studies demonstrating the level of modern research and the characteristic range of objects. The publications included in the Table can be divided into two groups—those carried out without taking into account the reflection intensities in the electron diffraction pattern for compounds (I)–(VIII) and those using them in order to carry out a complete structural analysis of compounds (IX)–(XXI).

In the studies of the first group, the determinations were made of the space group, of the unit cell parameters, and of the packing elements and, for compounds (II)–(IV), (V), and (VIII), the hypothesis concerning the chain conformation was justified. The value of studies of this kind consists primarily in the fact that the structures of the compounds investigated cannot be studied by X-ray diffraction because neither oriented specimens nor sufficiently large crystals can be obtained for such compounds. Polymers of this type include poly(*p*-oxyphenylene-*m*-carbaboranyl),[39] poly(dipropylsiloxane),[40] and also weakly orientable poly(diarylsiloxanes).[41] All the polymers enumerated were first investigated with the aid of EMD. Poly(vinylidene fluoride) had been studied earlier by X-ray diffraction but the controversy concerning the structure of its γ-form extended over a decade and it was shown that mechanical deformation leads to a polymorphic transformation (the transition from the γ-form to the β-form). The study of single crystals with the aid of the electron microscope, which rules out the necessity for the mechanical deformation of the specimen, made it possible to determine unambiguously the structure of the γ-form and also to observe the phase transition to the ε-form on thermal annealing of crystals of the γ-form.[42]

Analysis of the examples presented in the Table shows that polymers whose properties have attracted attention have been most often the objects of electron microscope studies. Such objects include, for example, the class of polyphosphazenes, forming liquid crystal systems, whose representatives are poly(bistrifluoroethoxyphosphazene) and poly(bisphenoxyphosphazene).[43] Poly(*p*-oxybenzoyl) also has interesting properties,[44,45] because its copolymers with other polyesters make it possible to obtain liquid crystal systems.[46,47] This polymer was first investigated in 1976, but the structure proposed for the double helix was not confirmed by other physical methods. A precision reinvestigation carried out in 1984 made it possible to correct the initial data and to determine unambiguously the crystal structure of the compound.[45]

In assessing the advances achieved with the aid of the EMD method in polymer chemistry on the basis of the results of compounds (IX)–(XXI) (see Table), one may conclude that this method permits crystal-chemical determinations whose aim is to establish the atomic structure and the molecular packing of high-molecular-weight compounds. A number of compounds of this group had been investigated earlier by the X-ray method. These include poly[3,3-di(chloromethyl) oxacyclobutane],[38] poly(ethylene sulphide),[14] cellulose triacetate,[48] poly(β-oxybutyroyl),[49] polyesters of terephthalic acid and aliphatic glycols,[13,15,51,52] and also *trans*-polyacetylene.[52] For these polymers, the results of EMD studies confirmed, revised, or supplemented the existing X-ray diffraction data. In other cases, the structure of the compound was determined for the first time by the EMD method, for example, those of poly(*p*-xylylene),[53,54] poly(1,4-*trans*-cyclohexanediyldimethylene succinate),[55,56] and poly(1,11-dodecadiyne).[57]

When the total structural analysis of the polymer by the EMD method is carried out, this problem is greatly facilitated in those cases where data are available for the structures of the individual fragments of the polymer unit and the way that they are linked together. The structures of low-molecular-weight compounds serving as models of the monomer units of the macromolecules have been determined for this purpose. For example, the structure of cellulose triacetate has been deduced from data on the structure of the trimer.[48] Dimethyl terephthalate and the diphenyl ethers of the corresponding glycols have been investigated as models of the units in polyesters.[15,49–51] An analogous procedure has been used in the study of poly(1,4-*trans*-cyclohexanediyldimethylene succinate).[55,56]

A number of the publications presented in the Table reveal very great advantages of diffraction electron microscopy in the study of polymorphism. Thus it has been found that the texture X-ray diffraction pattern of poly(hexamethylene terephthalate) contains reflections from several polymorphic phases which are superimposed and cannot therefore be used to establish the structure of each of these phases. On the other hand, in the study by the TEM method the crystals of each phase have their own characteristic form and give rise to an individual EMD pattern; furthermore, in the polymer

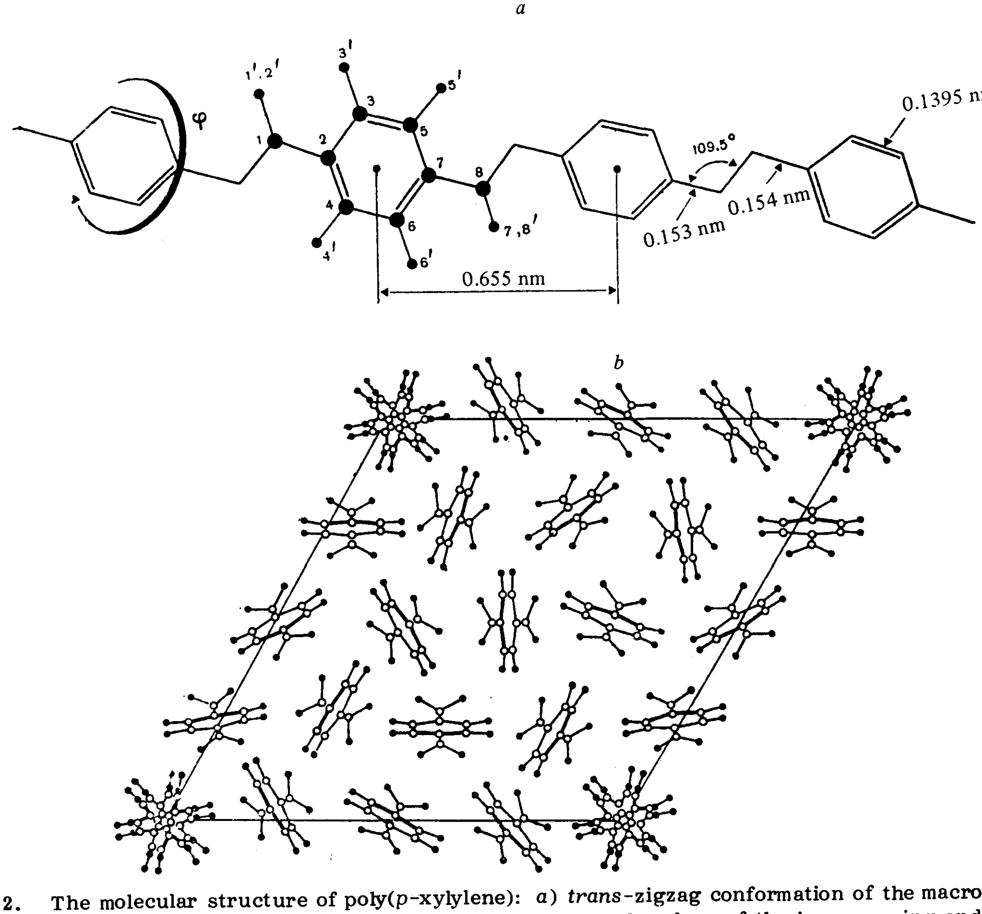

Figure 2. The molecular structure of poly(*p*-xylylene): *a*) *trans*-zigzag conformation of the macromolecule with a repeat period of 0.655 nm; $\phi = 90°$ is the angle between the plane of the benzene ring and the plane of the $-CH_2-CH_2-$linkage; *b*) three-dimensional structure of a single crystal of the β-form in projection onto the basal plane; the filled and open circles denote carbon and hydrogen atoms respectively; the unit cell contains 16 macromolecules, one of which assumes one of three equivalent positions in accordance with the *P*3 symmetry.

phase I it is possible to distinguish two similar structures. Separate analysis of electron diffraction patterns of single crystals made it possible to characterise all three polymorphic phases [(XIV)–(XVII), Table] and to index fully the reflections on the X-ray diffraction pattern. The problem of isolating one of the polymorphic phases has been solved also for poly(*p*-xylylene) [(XVIII), Table] in an investigation by Japanese workers,[53,54] which demonstrated the high level of the advances in the application of TEM to the study of polymers. Electron microscopes of two types were used—with a potential of 80 kV (JEM-7) and a high-voltage microscope (JEM-500). In both cases images of both the microstructure and of the EMD pattern were obtained (Fig.1). The structure of the β-form with an *R*-factor of 0.21 was analysed on the basis of quantitative microdiffraction data; the application of the high-voltage instrument enhanced the local nature and the resolution of the EMD patterns and also reduced the radiation damage during the recording of the pattern. A series of focal photomicrographs with a resolution of 1.5–2 Å were obtained. The photomicrographs, representing a direct resolution of the crystal lattice of the β-form, were treated by the optical filtration method. The optical diffractometer trace for the image coincided with the EMD pattern of the single crystal.

The resolution of the interplanar spacings on the photomicrograph was achieved for polydiacetylene single crystals on the basis of 1,6-di(*N*-carbazolyl)hexa-2,4-diyne[58] and also poly(*p*-phenyleneterephthalimide).[59] However, only in the case of poly(*p*-xylene) did the combination of the analysis of the high resolution image and the EMD patterns lead to the determination of the chain conformation and the atomic coordinates and to the discovery of the characteristic features of the molecular packing in the crystal (Fig.2).

The methodological procedures in the crystal-chemical determinations of the structures of polymeric compounds are extremely individual and depend to a large extent on the complexity of the structure of the object and the completeness of the available experimental data. A general approach to the solution of the problem usually involves the conformational analysis of the postulated model, which makes it possible to determine the chain parameters influencing the repeat period and also the internal energy of the system. Then the conformation in best agreement with experimental data is selected by trial and error. Apart from conformational analysis the Fourier synthesis of the electron density has been used, for example, by Claffey et al.[38] and Roche et al.[48]

The model is refined by the method of least squares, familiar from X-ray diffraction, modified for the determination of the structure of the macromolecule by introducing stereochemical limitations.[60,61] The method involving the minimisation of the packing energy[62] and the combination of the two methods mentioned[63] are also used. The *R* factor defining the agreement between the calculated theoretical and experimental structural diffraction amplitudes in accordance with the formula[8]

$$R=\sum_{hkl}\|\Phi_e|-|\Phi_t\|\Big/\sum_{hkl}|\Phi_e|,$$

where Φ_e are the observed structural amplitudes and Φ_t are the theoretical structural amplitudes for the proposed model, serves as the criterion of accuracy.

As can be seen from the corresponding columns in the Table, in modern studies the *R* factor is approximately 0.3 to 0.2, which indicates a fairly high accuracy of the results, bearing in mind the complexity of the macromolecule as an object of structural study.

Much attention has been devoted in studies of compounds (IX)–(XXI) to the validity of the application of the kinematic approximation to the calculation of structural diffraction amplitudes. Claffey et al.[38] proposed the agreement between the results of EMD and X-ray diffraction and also a weak influence of dynamic scattering on the R factor in test calculations as validity criteria. In a special appendix to a communication concerning the study of the structure of poly(1,4-*trans*-cyclohexanediyldimethylene succinate),[56] it was shown that ideal single crystals 100 Å thick are bent by not more than 2° and that dynamic scattering exerts only a weak influence on the *R* factor. In a study of poly(hexamethylene terephthalate), no bending of the crystals whatever was observed.[50] Under these conditions, the kinematic theory is fully applicable.

It must be emphasised that, in selecting the section for microdiffraction study, it is essential to employ a combination of the light field and the dark field modes of the operation of the electron microscope in order to choose suitable crystals. In the studies quoted above special attention was devoted to the reproducibility of the experimental results and to the accuracy of the measurements of the intensities. For this purpose, several tens of EMD patterns were photographed and the intensities were measured with the aid of automatic scanning microphotometers.

IV. THE PRACTICAL VALUE OF THE RESULTS OF STRUCTURAL STUDIES ON POLYMERS

Analysis of publications on the structural analysis of polymers by the EMD method has shown that in such investigations the authors endeavour to relate the characteristics of the structure of macromolecules to the physicochemical properties of the materials. Thus in a study of poly(trimethylene terephthalate), it was established[15] that the aliphatic fragment of the chain has the *trans*, *gauche*, *gauche*, *trans*-conformation and that the transition from the *gauche*-to the *trans*-conformation does not require much expenditure of energy, which accounts for the high capacity of this material for orientational stretching. As a result of a study of tolyl-substituted poly(diarylsiloxanes), it was found[41] that, with increase in the number of substituents in the benzene ring, the crystallographic cell parameters are altered, which increases the interchain distance; in its turn, this improves the solubilities and lowers the melting points of the materials.

A characteristic example of the direct relation between the structural results and the solution of problems of practical importance is provided by the study of the structure of polyacetylene. It has been shown that the conductivity of the material depends on the ratio of the *cis*- and *trans*-isomers and that only the latter isomer is thermodynamically stable.[52,64] Evidently, the knowledge of the structural characteristics of each isomer is extremely important for the solution of the problem of the specific influences on the properties of the materials in the synthesis of the polymer and its subsequent doping. However, the X-ray diffraction data obtained are controversial because of the thermodynamic instability of the *cis*-isomer and also because of the dependence of the structure of the compound on the polymerisation catalyst used. Furthermore, polyacetylene films cannot be made into highly oriented objects, which limits the scope of X-ray diffraction.

The electron microscope method provides much more information in the study of the structure of polyacetylene, since it makes it possible to carry out its formation reaction directly on the electron microscope grid, the fibrillar crystals giving rise to a high quality texture electron diffraction pattern. The first studies on these lines were performed in 1980.[65] Then Shimamura et al.[52] were able to carry out a complete structural analysis and to obtain the crystallographic characteristics of the *trans*-isomer (XVII) (see Table), which were then confirmed also in other investigations.[66,67] In

1984 Dickenson et al.[68] studied the isomerisation of polyacetylene directly on the electron microscope grid and proposed a method for the determination of the *cis–trans*-isomeric composition of the polymer with the aid of EMD patterns. Simultaneously with the study of the structure of polyacetylene, the investigation of the doped materials by the EMD method was begun. Analysis of the studies on polyacetylene shows that, although they have not yet been completed and the structural data are so far contradictory,[69] nevertheless the electron microscope method is irreplaceable in the investigation of the initial polymer and of the conducting materials based on it.

Yet another example of the large amount of information derivable by the microdiffraction method is provided by the investigation of the solid-phase polymerisation of diacetylenes. The structural analysis of poly(dodeca-1,11-diyne) and of the insoluble product obtained by its γ-irradiation has been carried out.[57] This study led to interesting conclusions about the mechanism of structure formation in the final product (XXI). Namely, it was shown that the reaction involving the cross-linking of the chains is of the solid-phase type, because a secondary product is formed following a slight rotation and migration of the molecules along the crystallographic *c* axis when the closest packing of the parallel layers of polymer chains is achieved. This was indicated by the absence of a change in the space group and by the decrease in the volume of the unit cell of the crystal.

An electron microscope study of polydiacetylene based on 1,6-di(*N*-carbazolyl)hexa-2,4-diyne has been carried out (using TEM, scanning EM, and high-resolution TEM), which made it possible to obtain crystallographic data and a direct image of the structural motif of the crystal.[58] Polydiacetylene based on 2,4-hexadiynylene bistoluene-*p*-sulphonate was investigated in solid-phase polymerisation on the electron microscope grid[70] and also directly in the chamber of the electron microscope.[71] In the latter case it was claimed that the results of the investigation are of practical interest for the preparation of photoresistors. An important structural result of the studies of the solid-phase polymerisation of diacetylenes is the demonstration of the formation of fully straightened chains distributed in the plane of lamellar and fibrillar crystals.[70]

An application of electron microscopy with practical importance involves the study of the structure of highly modular thermostable fibres of the type of poly(*p*-benzamide)[59] and poly(*p*-phenylenebenzothiazole).[72] The crystal structures of these compounds have been investigated, by X-ray diffraction, but the joint application of scanning and transmission EM (the light and dark field of modes, EMD) also helped to elucidate the structural organisation of these materials which determines their unique properties.

Thus one may conclude that the importance of the microdiffraction method consists not only in the determination of data on the structures of the crystalline regions of polymers, but also in the possibility of using the structural results for the solution of applied technological problems.

V. MODERN SOLUTIONS OF EXPERIMENTAL PROBLEMS INVOLVING THE APPLICATION OF THE ELECTRON MICRODIFFRACTION METHOD TO THE STUDY OF POLYMERIC COMPOUNDS

The success of the structural analysis of polymers depends in many respects on the solution of a series of experimental problems, such as, for example, the preparation and correct recording of data for the test objects. As shown above, electron diffraction patterns of single crystals have the highest information content (based on the resolution of the reflections and their intensities). A general method for the preparation of single crystals involves crystallisation from solutions and systematic studies of the structures of polymers were begun with its aid.[31–33] In the Soviet Union this field was pioneered by members of Kargin's School.[73–75] Various methods of crystallisation from solutions were developed by the end of the 1970's. These methods are characterised by two main procedures: the use of highly dilute solutions (0.001–0.1%) and rigorously controlled crystallisation temperatures. The long crystallisation period, necessary for the preparation of perfect crystals, is noteworthy (for example, several days in the crystallisation of polyacrylonitrile[76] or even several weeks in the case of isotactic polystyrenes[77]). Even readily crystallising polymers, such as, for example, poly(*p*-xylylene) (XVIII) (see Table), have to be maintained at the crystallisation temperature for several days.

The method and mechanism of crystallisation from solutions have been examined in greatest detail in the paper of Blundel et al.[78] and in Keller's review.[79] It was shown that, in the course of repeated dissolution and precipitation of polymers, a crystallisation "memory" is retained in the form of the spontaneous formation of nuclei on which the macromolecules are recrystallised. There exists a limiting redissolution temperature at which the crystals formed have a monolayer character with a perfect habit and a uniform thickness even at a relatively high concentration of the initial solution (0.1%), although an increase in concentration usually complicates the morphology of the supermolecular formations. For example, the temperature of the primary dissolution of polyethylene in xylene was 120 °C and was determined visually from the transparency of the solution and by dilatometric measurements. On cooling to 75 °C, exhaustive crystallisation occurred with appearance of turbidity in the solution, which again became transparent at 98 °C. Repeated isothermal crystallisation at temperatures in the range 98–105 °C led to the formation of perfect crystals giving rise to a distinct EMD pattern. This method is general for the crystallisation of polymers from solutions, naturally with an individual selection of crystallisation temperatures. It has been used in studies on the crystallisation of compounds (IV), (V), and (IX)-(XVI).

For polymers which are readily soluble in organic solvents and which are not precipitated from the solution on cooling, hot concentrated solutions are mixed with a suitable amount of precipitant. This procedure was proposed in early studies[58,59,80] and is again used nowadays, for example, in the preparation of polymers such as derivatives of polyphosphazene (VI) and (VII) (see Table). A difficult feature of the method is the need to eliminate the possibility of contact between the polymer and an excess of the precipitant, which is achieved by rigorous stirring or by breaking the tube with the solution in the flask containing the precipitant. Polymers also crystallise when solutions are cooled very slowly, for example, at a rate of 0.5 K h^{-1} and less, as was done in the crystallisation of poly(ethylene terephthalate).[81]

In carrying out crystallisation from solution, one should bear in mind that polymers can form solvates with the solvent.[82,83] A specific feature of the solvates is the breakdown of their crystal structure after the removal of the solvent or after its replacement by another liquid, as a result of which the diffraction patterns of the electron microscope preparation vanish.[64,84] In order to rule out the possibility of the formation of solvates in the preparation of perfect polymer single crystals, it is necessary to use mixtures of a poor solvent with the precipitant and a high crystallisation temperature. It is then also essential to subject the suspensions to hot filtration with subsequent drying *in vacuo*.[85]

A simpler method of preparation of single crystals has been proposed.[66,86] It actually consists in isothermal crystallisation from a dilute solution in an atmosphere of the solvent itself. The authors of these investigations obtained polyethylene, polypropylene, isotactic polybut-1-ene, polyacrylonitrile, and cellulose triacetate single crystals in the following manner: a glass plate attached to a string was lowered vertically into a thermostatted solution of the polymer and, after being kept there for a short time, was removed with the aid of a mechanical device at a rate of 1 cm h^{-1}; after it had risen fully, the plate was kept for a further 1 h in the solvent vapour, the polymer film was transferred to the surface of water by a standard method, and was fished out onto the grid holder. This method has not come to be widely used but it has been tested successfully on a series of polymers, for example, in the crystallisation of carbaborane-containing polyesters and polydiarylsiloxanes (I), (III), and (IV) (see Table).

The preparation of electron microscope objects, synthesised by solid-phase polymerisation, is also closely related to methods of crystallisation from solution. The question of preparing almost defect-free polymer single crystals by the topochemical polymerisation of diacetylene derivatives has been examined in a review,[87] which also includes electron microscope results. The usual method of preparation of the objects [for example, compound (XIX)—see Table] involves the initial growing from the solution of perfect monomer crystals in the form of lamellae[57] or needles,[59,69] which are deposited on a grid holder with a carbon support and are then subjected to various types of treatment to polymerise them, for example γ-irradiation from a ^{60}CO source. Similar methods have been used in the preparation of polyacetylene (XX) specimens (see Table): a solution of the catalyst is deposited on the grid with the support, dried, cooled to −78 °C, and maintained in a stream of acetylene at a pressure of 3–5 mmHg for 20 s; the *cis*-isomer is converted into the *trans*-isomer by heating the object on the grid at 200 °C for 2 h.[52]

In the preparation of crystals from solution, an extremely important stage involves the deposition of the object on the grid holder, because kinematic scattering conditions break down not only when the thickness of the crystals increases but also when they are bent. It has been shown that the best support for the preparation may be a thin carbon film, although it does in fact increase the diffuse background on the image and on the EMD patterns.[52,54] The orientation of the crystals on evaporation of the solution can be specified by the surface of the base, for example, the cleavage surface of NaCl or mica. A precision study by this method has been carried out[42] [compound (V)—see Table]. It was shown that, in the thermal crystallisation of poly(vinylidene fluoride), epitaxial growth in two mutually perpendicular directions is observed on the NaCl surface. Analysis of the EMD patterns of the object crystallised on mica and on the NaCl surface, with the aid of goniometric measurements, yielded information for the most accurate determination of the crystallographic parameters of the γ-phase.

As already stated in Section II, the texture electron diffraction patterns of films or fibres can be used in addition to the electron diffraction patterns of single crystals for the determination of the crystal structures of polymers. The development of methods for the orientational crystallisation of thin polymer films was dictated not only by the need to determine the molecular structure but also by the possibility of investigating the supermolecular structures of partly crystallised specimens under low-angle diffraction conditions. We shall not deal with this field of study, but procedures for the preparation of oriented crystalline specimens for electron microscopy have been described.[88–90]

The methods of preparation of thin oriented films have been described for poly(vinylidene fluoride),[91–93] poly(alkaneimides),[16] poly(diarylsiloxanes) [compounds (III) and (IV)—see Table] and poly(ethylene sulphide) (X). In the main, the preparation of the specimens reduces to casting thin films from dilute solutions (0.5–0.25%) and their monoaxial stretching with simultaneous or subsequent annealing at a temperature close to the glass point. This procedure involves considerable experimental difficulties in view of the small thickness (and hence low strength) of the films. Miniature devices in the form of frames of different design, to which the films are attached by adhesion on being withdrawn from water, are used for stretching. Devices for stretching in the microscope itself have also been proposed.[94] It is noteworthy that many investigations prefer to use the primitive method involving the stretching of the films on water with the aid of forceps[95] or on glass in a softened state with the aid of a spatula. For example, during this preparation procedure, it has been possible[14] [compounds (X)—see Table] to obtain the EMD pattern of a film of crystalline oriented poly(ethylene sulphide), which was suitable for complete structural analysis (in combination with electron diffraction patterns of single crystals). The polymer can also be subjected to deformation not only by stretching the specimen but also by shear, as has been done, for example, in the study of poly(*p*-phenyleneterephthalimide)[96] and also polyacetylene.[97]

Whereas the preparation of oriented crystalline films presents major difficulties to the investigator, the study of the structures of crystalline fibres is greatly facilitated, since in this case one can use the ultrasonic dispersion method with subsequent deposition of the object on grid holders with a support. Dispersion methods and devices have been described in practical manuals.[98] As an example of the use of dispersion in EMD studies, one may quote the investigations of highly modular thermostable fibres.[59] An unexpected result was obtained in the preparation of a poly(*p*-oxybenzoyl) (VIII) specimen, where the dispersion of the initial powder made it possible to observe in the electron microscope both polymer crystals and fibres giving rise to a texture electron diffraction pattern.

In addition to the methods described, mention should be made of the preparation of replicas and subsequent removal of the test substance, which had been proposed already at an early stage of the development of electron microscopy[99,100] and has been used successfully in modern research.[101]

Apparently the most complex method for the preparation of polymer specimens involves the use of an ultramicrotome, because it can be accompanied by the mechanical deformation of the specimens and the introduction of artefacts into the investigation. This method has been developed mainly for the study of biological objects and has been described in special manuals.[102] One of the first objects investigated by the EMD of thin sections was carbon fibres.[103] It was found that a suitable casting material for the fixation of the polymer specimens in the ultramicrotome holder is molten sulphur.[104] However, at present organic polymers are fixed with the aid of casting materials based on epoxide compositions and cryo-ultramicrotomes are used for the preparation of sections.[105,10 It is noteworthy that hitherto the method of EMD of sections has been used to investigate the local order in the specimen; there have been no publications on structural analysis using this technique.

Examination of the methods of preparation of polymer objects for microdiffraction studies shows that in many cases this procedure can introduce artefacts associated, for example, with the influence of the rate of evaporation of the solvent, random deformation, etc. These processes must be investigated in order to eliminate the artefacts and to make the results of the investigation more correct. On the other hand, phenomena of this kind are also studied specially in order to reveal a whole series of properties of polymers and in this respect electron microscopy has a considerable scope. Overall, the literature data show that there is no universal method of preparation of polymer specimens. Each object requires an individual approach and considerable preparatory work in order to select the correct conditions and success depends in many respects on the skill of the experimenter.

The problem of protecting the polymer specimen from radiation during focussing and photography merits special attention not only from the standpoint of the reliability of the diffraction data but also from the standpoint of the very possibility of such an investigation. This is especially important when the goniometric method is used, where, in the course of the short lifetime of the crystal, it is necessary to rotate the specimen in order to obtain a three-dimensional diffraction pattern, as has been done, for example, in studies of compounds (V) and (XII)–(XVI) (see Table).

One of the causes of damage to the specimen by the electron beam is ionisation and excitation of atoms and molecules, as a consequence of which the initial equilibrium state of the substance breaks down. There are special publications on this question in the literature.[107] The mechanism of the effects of irradiation on organic objects has not been finally elucidated but it has been established in relation to polymers, for the maximum irradiation dose, which is specific to each polymer, that the specimen is fully converted into an amorphous form while the morphology of the supermolecular formations is retained.[79,108] The sensitivity of the polymer specimen to irradiation is associated with its chemical structure. In particular, as aromatic fragments accumulate in the macromolecule, the resistance to irradiation increases. Thus, it has been found that crystals of poly(*p*-xylylene) are fully converted into an amorphous form in an electron microscope with an accelerating potential of 500 kV for an overall irradiation dose exceeding by a factor of 20 that for polyethylene.[54] Polymers with a higher resistance to irradiation can be successfully investigated by the EMD method, but it has been shown by a number of workers that objects sensitive to irradiation are also susceptible to electron diffraction observations and special precautions are taken against damage [compounds (XII)–(XVI)—see Table].

The method of protecting the object is to reduce to the maximum extent the intensity of the electron beam and also to shorten the residence time of the specimen under irradiation, especially the exposure time. The procedures for the protection of the object against irradiation have been examined in extremely great detail by Dobb et al.,[109] who suggested that a special disc covering the central portion of the beam during the focussing of the image be inserted in the aperture holder of the second condenser. On the other hand, the exposure of the object to the electron beam entails the appearance of carbon contaminations, which reduce the information content of both the image and of the electron diffraction pattern as a result of the enhancement of the diffuse scattering background. The question of the nature of the contaminations and of the methods of dealing with this phenomenon is considered in special manuals[98] (p.25). Devices for cooling the object to the temperature of liquid nitrogen are constantly used in studies involving the measurement of reflection intensities for protection against irradiation [compounds (IX) to (XXI)—see Table]. Such devices are present in all modern microscopes.[1] The use of highly sensitive photographic emulsions plays an important role in diminishing the exposure time during photography. The latest transmission electron microscopes are fitted with devices which make it possible to reduce the period during which the electron beam acts on the specimen with the aid of two pairs of deflecting systems.[1] The use of high-voltage microscopes makes it possible to enhance the local nature of the diffraction and also to reduce the exposure time.

However, the problem of protecting the specimen against irradiation has been solved most radically with the aid of a new technique of diffraction studies developed towards the end of the 1970's, which consists in the joint use of transmission of and scanning with an electron beam having a small diameter.[110–112] Whereas in the usual TEM the size of the irradiated part of the object is determined by the diameter of the selective diaphragm located below the object holder and amounts to ~1 μm or more, in the scanning-transmitting EM the beam diameter is itself limited and the diffraction area, determined by the diameter of the probe, can be reduced to 300–100 Å. The new method used in the scanning-transmitting electron microscope permits an enhancement of the local nature of the diffraction, an increase of its resolution, and the maximum protection against irradiation of the parts of the object adjoining the test region, as has been demonstrated in a study of polyethylene.[110] An example of the use of this method for the study of crystal structures is provided by the investigation of poly(*p*-oxybenzoyl) (VIII) (see Table).

Overall, the results of modern studies on diffraction EM have shown that, although the problem of protecting the polymer against irradiation requires constant attention, nevertheless it is not an obstacle to the use of the given method in the structural analysis of high-molecular-weight compounds.

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The review of publications on the electron microscopy of polymers permits the conclusion that this method has advanced appreciably not only in connection with the development of high-resolution instruments but also as a consequence of the development of methods for the quantitative analysis of electron microdiffraction patterns. However, one must also conclude that the structural analysis of polymers with the aid of TEM has still not become a standard procedure. The reason for this is the inadequate availability of improved electron microscopes and also the difficulties in the preparation of the specimens and in the interpretation of electron microscope data. As regards the interpretation of visual high-resolution TEM images, it is useful to bear in mind the words of Kabayashi, the renowned specialist in this field, that to see in the electron microscope does not necessarily mean to believe.[113]

The determination of the crystal structures of polymers requires their combined study by means of several independent methods, among which electron microdiffraction plays an important role. The accumulation of experience concerning the application of EMD and the continuing improvement of the instrumental technique undoubtedly open up prospects for the development of electron microscopy up to a readily accessible standard method for the structural analysis of high-molecular-weight compounds.

During the preparation of the review for printing, a series of communications, both methodological and of a review character, concerning the use of electron microscopy for the structural investigation of polymers were published. Thus a method has been developed[114] for the epitaxial growth of polyethylene crystals in order to obtain and analyse EMD patterns. The same workers in another communication[115] analysed in detail the possibilities of the epitaxial method for the quantitative EMD analysis in comparison to crystallisation from solutions; the comparison was carried out in relation to a series of polymers, especially biological polymers.

Review data on the use of the EMD method in polymer chemistry have been included in the publication by Dorset.[116] The advances of electron microscopy in securing quantitative information about the structure and composition of polymers have been described in a review[117] which deals with problems of the use of spectroscopic-analytical information and also with the protection of the test object against damage by irradiation. A novel microdiffraction method involving the shift of the aperature diaphragm, which replaces, in the authors' view, the goniometric technique, has been proposed.[118]

Data on the structure of poly(butylene terephthalate) and of its block copolymers have been obtained by the EMD method in the scanning-transmission mode.[119] The structure of poly(3-hydroxybutyrate) has been determined.[120] Studies by Japanese workers, using the entire range of the diffraction and visual possibilities of high-voltage TEM, have been continued—in particular, the structures of a conducting polymer, namely poly(1,4-phenylene),[121] and also of isotactic polystyrene[122] have been studied.

The results of the studies quoted above demonstrate the continuously increasing contribution of the microdiffraction electron microscope method to the crystal-chemical research into high-molecular-weight compounds.

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Polyorgano-polysiloxane Block Copolymers

I.M.Raigorodskii and E.Sh.Gol'dberg

The literature data on the principal methods for the synthesis of polyorgano-polysiloxane block copolymers incorporating carbochain and heterochain organic fragments are examined and surveyed. It is shown that the microphase separation, associated with the differences between the chemical natures of the blocks, exerts a decisive influence on the morphological, physicochemical, and mechanical properties of such block copolymers. The wide scope of the applications of polyorgano-polysiloxane copolymers is demonstrated.

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I. INTRODUCTION

One of the problems in polymer chemistry of current interest involves the development of methods of synthesis and the study of the properties of a relatively new class of polymeric materials—block copolymers. Linear copolymers having the structure $(AB)_n$, in which the contributions by blocks of different nature create a set of specific properties, are of considerable interest in this connection. On the other hand, the introduction as one of the blocks into such copolymers of a polyorganosiloxane, which is characterised by a low glass point, good chemical, hydrolytic, radiation, and thermal stabilities, a high permeability to gases, a weak temperature dependence of its physicochemical properties, a low surface tension, a pronounced hydrophobic character, and a high frost resistance, makes it possible to obtain materials with properties of practical value.

The thermodynamic incompatibility of the organic and organosilicon blocks leads to the appearance in such systems of microphase separation, which makes it possible to regard them as pseudo-filled systems. The physical network arising under these conditions increases the deformation-strength characteristics and influences the physicochemical properties of block copolymers. The above features of polyorgano-polysiloxanes permit the segregation of these block copolymers as a separate group of polymers.

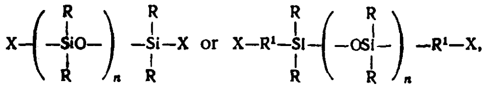
Polyorgano-polysiloxane block copolymers are of special interest for biology and medicine. The stability of these materials in biologically active media is high, they are readily sterilised, exhibit high haemo- and tissue compostibility, are resistant to ageing and the action of microorganisms, are optically transparent, and are permeable to vapours and gases. Such block copolymers can be used as implants of different rigidity, which can be achieved by regulating the composition of the copolymer.

In the reviews devoted to block copolymers published hitherto,[1-5] siloxane-containing copolymers incorporating carbochain and heterochain organic fragments have been examined. However, these publications deal with only certain individual examples of the synthesis and investigation of the properties of linear polyorgano-polysiloxane systems. We thought it timely to survey in the present review the available literature data on siloxane-containing block copolymers.

II. METHODS OF SYNTHESIS OF POLYORGANO-POLYSILOXANE BLOCK COPOLYMERS

Two main methods of synthesis of block copolymers containing siloxane fragments have now been proposed.

1. Polycondensation of organic oligomers, synthesised beforehand, with silicon-containing oligomers having the structure



$$X-\left(-\underset{R}{\overset{R}{Si}}O-\right)_n-\underset{R}{\overset{R}{Si}}-X \text{ or } X-R'-\underset{R}{\overset{R}{Si}}-\left(-O\underset{R}{\overset{R}{Si}}-\right)_n-R'-X,$$

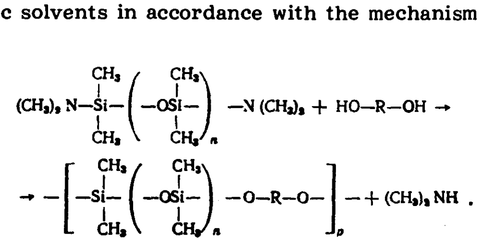
where R,R' is a carbon containing group and X is a functional group (hydroxy-, halogeno-, amino-, aminoalkyl, carboxy-, etc.).

2. Methods based on the use of cyclic organosiloxanes.

The principal methods of synthesis of linear oligomers and cyclic organosiloxanes have been examined in detail in monographs.[6-8] Depending on the nature of the initial components, block copolymers containing Si–C, Si–O–Si, Si–O–C, and Si–N interblock linkages have been described.

Polycondensation with Participation of αω-Bis(dialkylamino)-oligosiloxanes

The commonest method of synthesis of polyorgano-polysiloxane block copolymers involves the interaction of αω-bis(dimethylamino)oligodimethylsiloxanes with organic oligomers in organic solvents in accordance with the mechanism



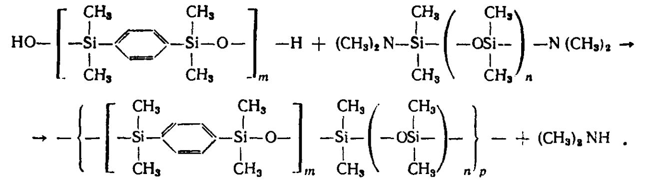
$$(CH_3)_2N-\underset{CH_3}{\overset{CH_3}{Si}}-\left(-O\underset{CH_3}{\overset{CH_3}{Si}}-\right)_n-N(CH_3)_2+HO-R-OH\rightarrow -\left[-\underset{CH_3}{\overset{CH_3}{Si}}-\left(-O\underset{CH_3}{\overset{CH_3}{Si}}-\right)_n-O-R-O-\right]_p-+(CH_3)_2NH\ .$$

The structure of the organic blocks in the copolymers obtained and the reaction conditions are indicated in Table 1.[9-26] The polycondensation results in the formation of regularly alternating block copolymers in which the molecular weight of the blocks is equivalent to the average molecular weight of the oligomers.

The dimethylamine evolved is readily removed and the reaction is therefore simple and effective and can be used to synthesise copolymer blocks of different lengths. However, the dimethylamine evolved can induce side reactions in the synthesis of copolymers containing ester linkages. It has been noted[11,25,27] that, when oligomers with a sufficiently high molecular weight are used, it is not possible to ensure reliably the equimolar reactant ratio, which leads to the formation of block copolymers with low molecular weights and a broad molecular weight distribution. In order to obtain block copolymers with a high molecular weight, it has been suggested that one of the components be gradually injected into the reaction zone; the character of the end groups and blocks of the copolymer then depends on the specific stoichiometry of the reaction. In order to avoid hydrolysis and homocondensation of alkylaminosiloxanes, the solvents must be carefully dried. The process temperature varies from 25° to 108 °C depending on the nature of the organic oligomer and the solvent employed.

When oligomers with aliphatic OH groups are used, the above reaction is much slower than with aromatic OH groups, as has been demonstrated in relation to dihydroxymethylstyrenes.[25,26]

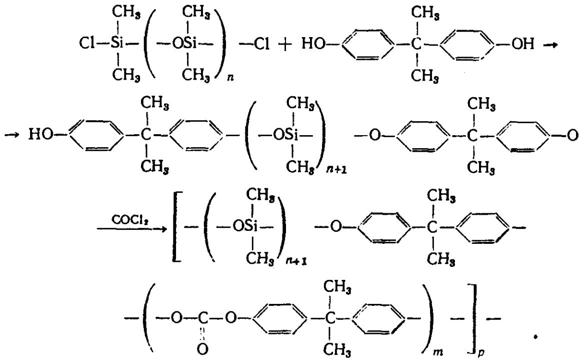
Dimethylaminosiloxanes have successfully used recently for the synthesis of polyblock polytetramethyl-*p*-silphenylene-siloxane-polysiloxane copolymers with a regular alternation of blocks:[28]



In the above example both oligomers contain silicon. However, it is useful to consider such systems in the present review because the principal features of polyorgano-polysiloxanes mentioned above can in fact be observed in them also.

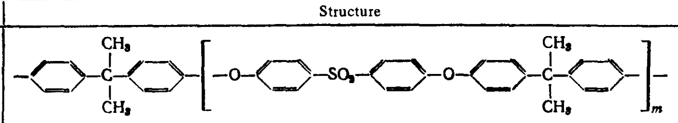
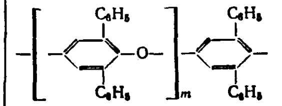
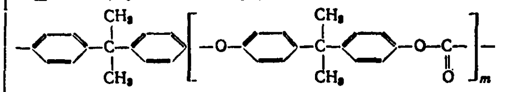
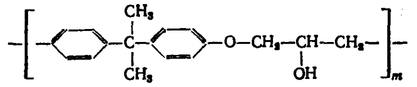
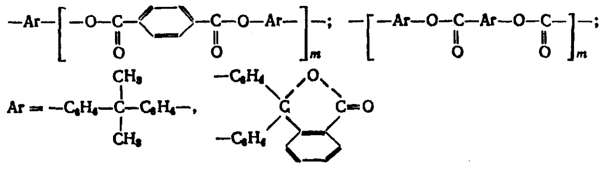
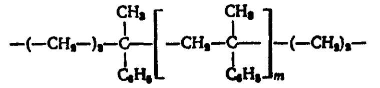
Polycondensation with Participation of αω-Dichloro-oligosiloxanes

Oligodimethylsiloxanes with terminal chlorine atoms are used mainly to synthesise polycarbonate-polysiloxane block copolymers. It has been noted[29–31] that the reaction of αω-dichloro-oligosiloxane with an excess of a bisphenol in solution in chlorinated hydrocarbons in the presence of a hydrogen chloride acceptor results in the formation of a αω-dihydroxy-derivative, which is treated with phosgene in the presence of an excess of the bisphenol until the attainment of the maximum viscosity of the reaction mixture:

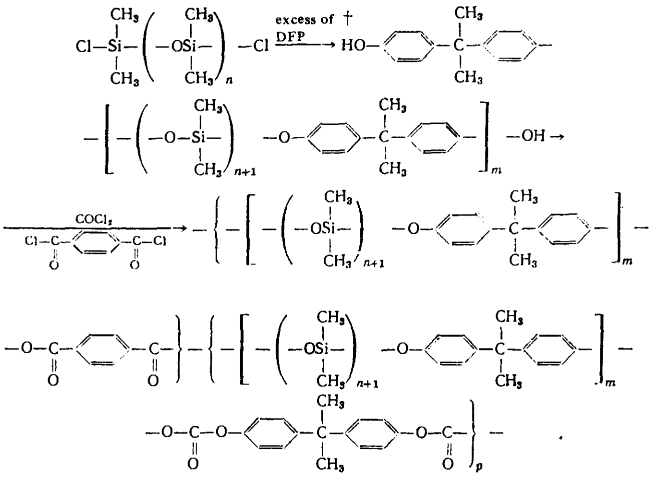


The resulting copolymer consists of statistically alternating polydisperse blocks and has a low molecular weight.

Table 1. The structure of the organic block and the conditions in the synthesis of polyorgano-polysiloxane block copolymers.

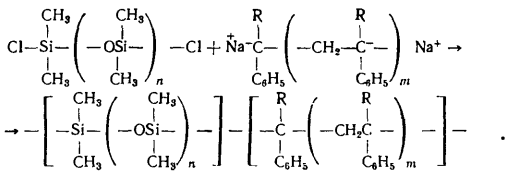
Organic block	Structure	T°, C	Solvent	Refs.
Polysulphone		25—120	Chlorobenzene, THF	[9—14]
Poly(phenylene oxide)		130	Chlorobenzene	[15—17]
Polycarbonate			Chlorobenzene	[18—20]
Polyhydroxyester		40—130	Methylene chloride, THF, chlorobenzene	[21]
Polyarylate		120—180	Trichlorobenzene	[22—24]
Poly-α-methylstyrene		120—180	Chlorobenzene, *o*-dichlorobenzene	[25—28]

The synthesis of a polyester-polysiloxane containing fragments of organic acids together with polycarbonate units has been described in a patent:[32]



In order to obtain block copolymers with a regular structure, it has been suggested that αω-dichloro-oligodimethylsiloxanes be condensed with oligomeric dihydroxycarbonates in solution in chlorobenzene in the presence of a tertiary amine (pyridine, triethylamine).[33-36] The molecular weights of the copolymer synthesised are 10^5.

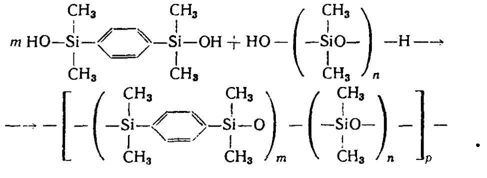
It has been shown[37,38] that the interaction of oligodimethylsiloxanes having terminal chlorine atoms with the disodioderivatives of styrene, α-alkylstyrene, or α-phenylstyrene in solution in tetrahydrofuran (THF) at room temperature can yield linear block copolymers:



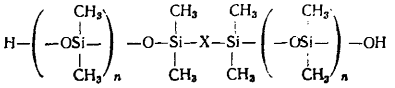
Polycondensation with Participation of αω-Dihydroxy-oligosiloxanes

The high mobility of the hydrogen atom in the hydroxy-group in dihydroxyoligosiloxanes makes it possible to use them for the synthesis of a whole series of block copolymers: polysilarylene-polysiloxanes, polyurethane-polysiloxanes, polyamidepolysiloxanes, and polyimide-polysiloxanes.

The synthesis of polysilarylene-polysiloxane block copolymers proceeds in accordance with the scheme



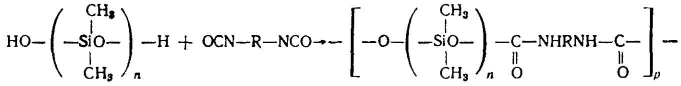
The reaction is carried out in solution in aromatic hydrocarbons at elevated temperatures in the presence of catalysts which do not cause a redistribution of units between siloxane blocks of different type, for example, tetramethylguanidine-bis-2-ethylhexanoate, N-hexylamine-2-ethylhexanoate, or a salt of formic acid and t-butylamine.[39-41] Since both initial components have the same functional groups, the condensation is statistical and the resulting high-molecular-weight copolymer contains blocks whose average length depends both on the ratio of the initial substances and on the molecular weight of the oligodimethylsiloxanes. Similar block copolymers with a more ordered structure have been obtained[42] by the reaction of diols having the formula



$$H-\left(-\underset{CH_3}{\overset{CH_3}{OSi}}-\right)_n-O-\underset{CH_3}{\overset{CH_3}{Si}}-X-\underset{CH_3}{\overset{CH_3}{Si}}-\left(-\underset{CH_3}{\overset{CH_3}{OSi}}-\right)_n-OH$$

[n = 0–1; X = 1,3 or 1,4-phenylene or the Y–Z–Y fragment, where Y = 1,3- or 1,4-phenylene and Z = O or OC(O)O] with phosgene in solution in pyridine.

Polyurethane-polysiloxanes can be obtained by polyaddition:



$$HO-\left(-\underset{CH_3}{\overset{CH_3}{SiO}}-\right)_n-H+OCN-R-NCO\rightarrow\left[-O-\left(-\underset{CH_3}{\overset{CH_3}{SiO}}-\right)_n-\underset{O}{\underset{\|}{C}}-NHRNH-\underset{O}{\underset{\|}{C}}-\right]_p-$$

The reaction is carried out in two stages: in the first stage, the hydroxylated oligodimethylsiloxane reacts with the organic diisocyanate, while in the second stage a "chain lengthening agent"—an organic diol or diamine—is introduced into the reaction mixture.[43,44]

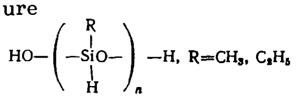
Prepolymers with terminal NCO groups, based on di- and poly-isocyanates and organic diols, can also be used as the organic component.[43,45,46]

It has been shown that the reactivity of oligosiloxane-glycols in urethane formation reactions is higher than that of aliphatic glycols,[47] which made it possible to synthesise successfully polyurethane-siloxane block copolymers containing alkylene bridges between the organic and organosilicon blocks.[48] Diamines,[49] organic oligodiols and oligodithiols,[50] as well as 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane[51] have been used as the "chain lengthening agents".

Polyester-siloxane-urethanes with polyester and polydimethylsiloxane blocks alternating statistically in the chain have been obtained;[52] the synthesis was carried out in one stage by introducing the intermonomer [di(4-isocyanatophenyl)methane or 2,2′-di-(*p*-isocyanatophenyl)hexafluoropropane] into a mixture of oligodiols [poly(ethylene glycol) or poly(ethylene glycol adipate) and αω-bis(β-hydroxyethoxymethyl)oligosiloxane] at elevated temperatures in solution in chlorobenzene in the presence of tin dibutyl-laurate as the catalyst.

Polyblock polyamide-polysiloxanes have been obtained by the reaction of dihydroxyoligodimethylsiloxane with an excess of terephthalic acid chloride and subsequent condensation of the resulting polyester with hexamethylenediamine;[53] however, it was not possible to achieve a high molecular weight of the polymer, whose intrinsic viscosity did not exceed 0.3 dl g^{-1}.

A method for the modification of polycaprolactam in the synthesis of polyamide by polyorganosiloxane compounds having the structure



$$HO-\left(-\underset{H}{\overset{R}{SiO}}-\right)_n-H,\ R{=}CH_3,\ C_6H_5$$

has been described.[54] The reaction yielded block copolymers containing siloxane linkages in the carbamide groups; an increase of the content of the organosilicon component in the

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†Excess of DFP (in Russian; Ref.32 states Me_3N in CH_2Cl_2) (Ed. of Translation).

reaction mixture above 2 wt.% inhibits the polarisation of caprolactam and impairs the physicomechanical characteristics of the block copolymer.

Treatment of a mixture of αω-bis(3-propoxy)oligodimethylsiloxane, di(hydroxyphenyl)propane, and terephthalic acid chloride in solution with phosgene afforded high yields of block copolymers with a high molecular weight.[32] The attempts to use oligosiloxanes with terminal hydroxypropyl and hydroxybutyl groups to synthesise polycarbonate-polysiloxanes by direct treatment with phosgene of a mixture of the oligosiloxane and di(hydroxyphenyl)propane under the conditions of interfacial condensation led to the formation of block copolymers with a statistical alternation of blocks and the degree of conversion of the oligodimethylsiloxane was low. Investigations[20,55] led to the discovery of the need for the preliminary treatment of the organosilicon oligomer with phosgene in order to obtain block copolymers having a high molecular weight and a high content of the organosilicon blocks. It is therefore useful to use the bischloroformates of oligomeric organosilicon diols in order to obtain polyorganopolysiloxanes by heterophase polycondensation.

Polycondensation with Participation of αω-Bis(chloroformato-organo)oligosiloxanes

The heterophase method of synthesis of block copolymers based on αω-bis(chloroformatoethoxymethyl)oligodimethylsiloxanes makes it possible to obtain high yields of regularly alternating polycarbonate-polysiloxanes[56] and polycarbonate-urethane-polysiloxanes with a unimodal molecular weight distribution (Fig.1) in accordance with the scheme[57,58]

Polycondensation with Participation of αω-Diamino-oligosiloxanes

These oligomers react readily at room temperature in solution or under the conditions of interfacial polycondensation with aliphatic and aromatic acid dichlorides[64] to produce high yields of high-molecular-weight soluble polyamide-polysiloxanes.

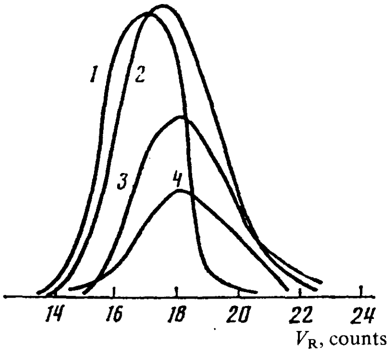
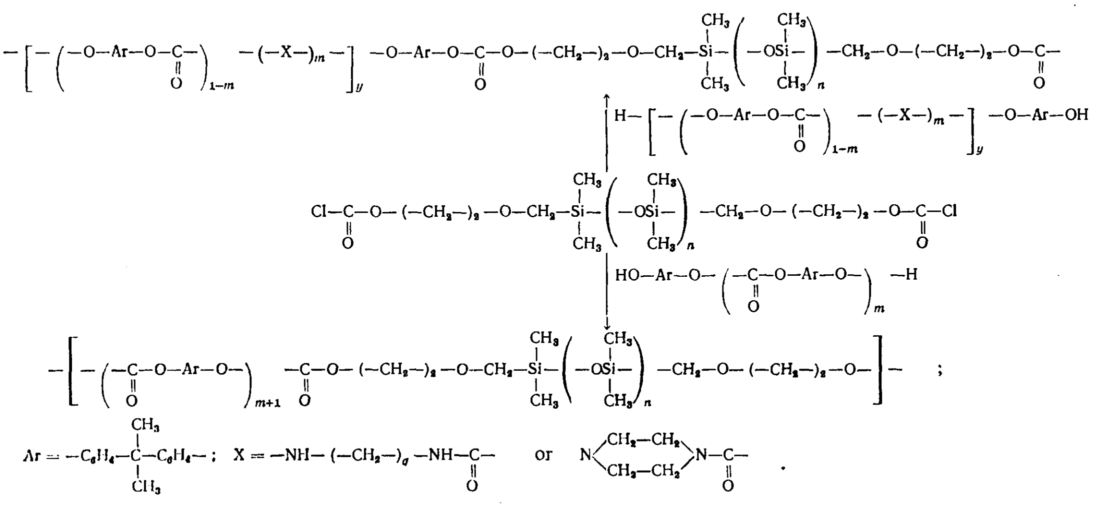


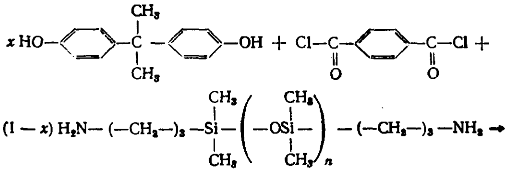
Figure 1. Chromatograms of polycarbonate-urethane-polysiloxanes with different compositions $N_{Si}:N_{CU}$: 1) 45: 6; 2) 45 : 10; 3) 45 : 3; 4) 45 : 2; N_{Si} = number of siloxane units, N_{CU} = number of carbonate-urethane units, and V_R = volume of eluent (one count = 2.5 ml).[58]

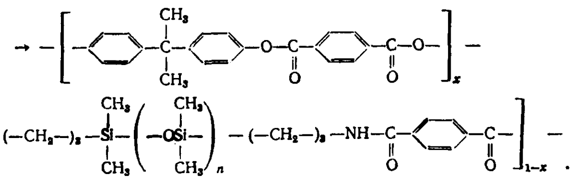


The bischloroformatosiloxanes presented in the scheme were used to obtain polyurethane-siloxanes in a heterophase system[59] and also copolymeric siloxane-carbonates[60] and siloxane-urethanes[61,62] with a statistical distribution of organic and organosilicon blocks.

Polyarylate-polysiloxanes have been synthesised by interfacial polycondensation to form αω-bis(chloroformato-organo)-oligosiloxanes and oligoarylate diols from phenolphthalein and di(hydroxyphenyl)propane.[63]

Polyamide-polysiloxanes containing polyarylate fragments have been obtained by the reaction[65]



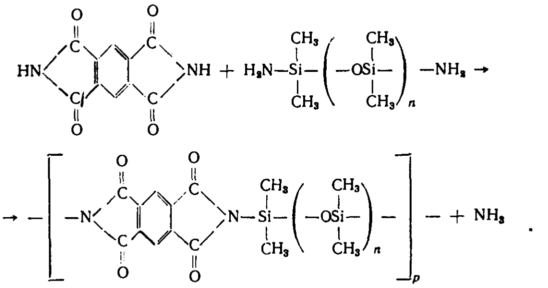


The yield of the target product is 80–90% and the intrinsic viscosity is 0.89 dl g^{-1}.

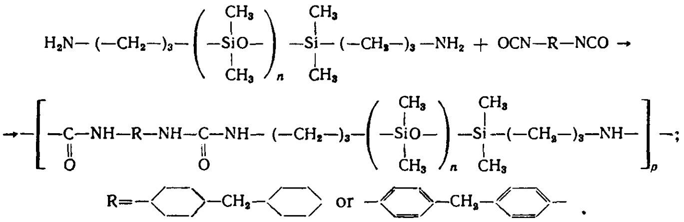
The reaction of oligodimethylsiloxane having terminal NH_2 groups with *N*-carboxyanhydrides of aminoacids of the type of DL-phenylaniline or γ-benzyl-L-glutamine in solution in chloroform at 200 °C leads to the formation of block copolymers of polysiloxane with polypeptides.[66]

Soluble polyimide-polysiloxanes have been synthesised by heating a prepolymer based on an excess of an aromatic dianhydride and an aromatic diamine[67] or the dianhydride of benzophenonetetracarboxylic acid[68] with aminoalkyl-containing oligodimethylsiloxanes.

The synthesis of polyimide-polysiloxanes whose nitrogen atoms are linked directly to silicon atoms has been described in a patent:[69]

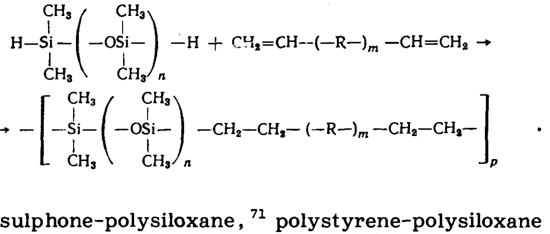


αω-Bis(aminopropyl)oligodimethylsiloxanes interact with an organic diisocyanate in 2-ethoxyethyl ether or THF with formation of polysiloxane-urea:[70]



Polycondensation with Participation of Oligosiloxanes having Terminal Silicon Hydride Groups

Copolymers with regularly alternating blocks have been obtained from oligodimethylsiloxanes having H–Si groups by the hydrosilylation reaction:



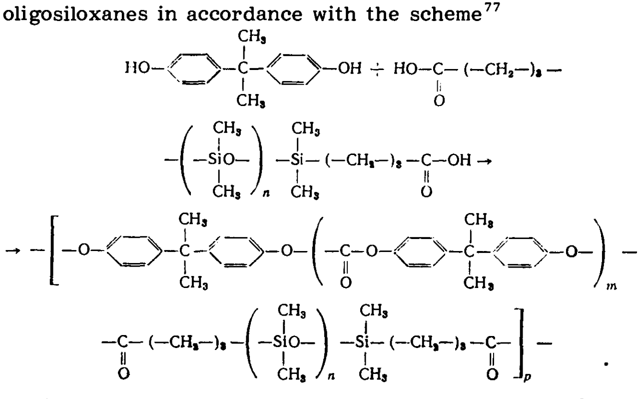
The polysulphone-polysiloxane,[71] polystyrene-polysiloxane and poly-α-methylstyrene-polysiloxane,[72,73] and polyurethane-polysiloxane[74,75] block copolymers have been synthesised by this method.

Despite the fact that the condensation conditions rule out side reactions and make it possible to obtain block copolymers with a high molecular weight, the reaction has not as yet found extensive application owing to the complexity and the multistage nature of the synthesis of the initial vinyl-containing organic oligomers and the need to employ expensive catalysts.

Polycondensation with Participation of Other Oligosiloxanes

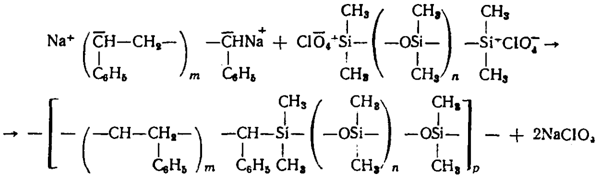
There are literature data on the synthesis of polyorganosiloxane block copolymers using oligodimethylsiloxanes having terminal acetoxy-groups. The process consists in the condensation of the terminal hydroxy-groups of polyester-urethanes obtained beforehand with the terminal acetoxy-groups of the oligosiloxane.[76]

The possibility of obtaining polyester-polysiloxanes by the heterophase condensation based on αω-bis(carboxypropyl)-oligosiloxanes in accordance with the scheme[77]



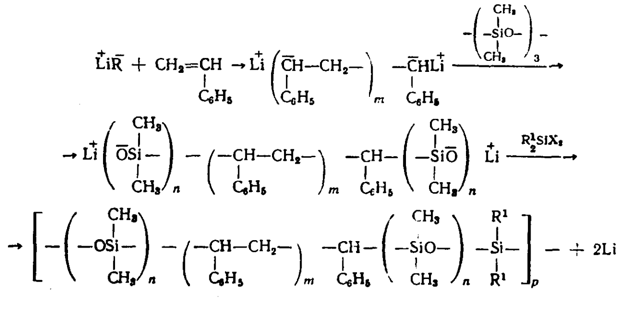
has been demonstrated. The authors note the need for the preliminary treatment of the oligosiloxane with phosgene to convert it into an acid chloride in order to increase the yield and the molecular weight of the copolymer.

Polystyrene-polysiloxane block copolymers containing regularly alternating blocks have been synthesised by the reaction of the oligostyrene anion with the oligomethylsiloxane cation in solution in THF:[78]



Reactions with Participation of Cyclic Organosiloxanes

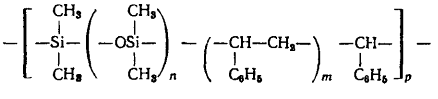
Polystyrene-polysiloxanes have been obtained by the joint anionic polymerisation of organosilicon cyclic compounds and styrenes:



The process includes the following stages: the polymerisation of styrene with a lithium initiator in the presence of a solvent (THF, benzene, or toluene) until "living chains" are formed, the introduction and polymerisation of hexamethylcyclotrisiloxane on such chains, and the joining together of the resulting blocks with bifunctional alkylsilanes.[79-83]

There is no chain termination in this process, which makes it possible to obtain a copolymer with a narrow molecular weight distribution. The block copolymer contains virtually no homopolymers nor cyclic compounds which failed to react. Dialkyldichlorosilane,[79-81] diacetoxydiphenylsilane,[82] and difluoromethyltrifluoropropylsilane[83] can be used as cross-linking agents.

In a modified synthetic scheme, the polysiloxane-polystyrene copolymer with terminal lithium atoms is treated with hydrochloric or acetic acid[81,84] to form blocks with terminal silanol groups. On further dehydropolycondensation in the presence of tin octanoate or caprylate, block copolymers having the following structure are obtained:



$$-\left[-\mathrm{Si}(CH_3)_2-\left(-\mathrm{OSi}(CH_3)_2-\right)_n-\left(-CH(C_6H_5)-CH_2-\right)_m-CH(C_6H_5)-\right]_p-$$

The copolymers of poly-α-methylstyrene with polydimethylsiloxane, containing short polystyrene[85] or α-alkylstyrene[86,87] blocks, have been obtained by analogous methods.

Polycarbonate-urethane-polysiloxane block copolymers can be obtained by the condensation in the melt of the oligocarbonate prepolymer with methylphenylcyclotrisiloxane in the presence of alkali metal hydroxides at 200–220 °C with subsequent interaction of the product with tolylene diisocyanate at 70–90 °C.[88]

Treatment of the oligocarbonate-siloxanediol synthesised in the first stage with methylphenylcyclotrisilazane in the melt at 180 °C yields polycarbonate-silazasiloxane block copolymers.[89] However, the process is complicated by the formation of isocyanate groups in side reactions, which are particularly vigorous for low molecular weights of the polysiloxane blocks. As a result of this, the block copolymers contain urethane linkages together with the polycarbonate and silazane blocks and have a branched or a cross-linked structure.

All the methods of synthesis of siloxane-containing block copolymers described above make it possible to obtain linear soluble products of different types with a predictable structure. The choice of particular conditions of synthesis permits the variation of the size of the blocks, the order in which they alternate, the molecular weight, the molecular weight distribution, and ultimately the properties of the polymers.

III. STRUCTURAL CHARACTERISTICS AND PHYSICOCHEMICAL PROPERTIES

1. The Morphology of Polyorgano-polsiloxanes

The chemical structure of the macromolecule influences the temperature dependent transitions, the chemical stability, the thermal stability, and the permeability of the block copolymers. However, the specific properties of elastoplastics, namely the elasticity, strength, and rheology of the solutions and melts, are determined by the morphology of the block copolymer and are the result of its structural heterogeneity, i.e. the incompatibility of the blocks leading to their separation into microphases.

The fundamental morphological model of silicon-containing block copolymers can be represented by a continuous matrix formed by a flexible siloxane block in which rigid blocks, associated into dispersed formations (domains) chemically linked to the continuous matrix, are distributed in a discrete fashion. The domains fulfil the function of the nodes of a chemical network or filler.[1]

The appearance of a two-phase supermolecular structure and the degree of separation into phases depend on the structure of the copolymer macromolecule and are determined by the degree of incompatibility of the components forming the blocks. A quantitative characteristic of the degree of incompatibility may be the difference between the solubility parameters of the constituent blocks of the polymer. The dependence of the degree of separation on the difference between the solubility parameters is illustrated by the quantitative correlation[90] between the solubility parameters of segments of polyorgano-polysiloxane block copolymers and their capacity for being worked in the melt (Table 2).

Table 2. The rheological characteristics of the block copolymers.[90]

Organic block	Δ*	Mouldability
Poly-α-methylstyrene	1,3	Good
Polystyrene	1,6	Good
Polycarbonate	2,2	Satisfactory
Polyarylate	2,6	Satisfactory
Polysulphone	3,3	Poor

*The difference between the solubility parameters of the blocks.

Table 2 shows that the smaller the difference between the solubility parameters of the rigid and flexible blocks of the copolymer, the more easily can it be worked in the melt. The explanation is that a large difference between the solubility parameters promotes an appreciable phase separation of the system even as far as the retention of a physical network in the melt, which significantly impairs the capacity of the copolymer for being worked. Microphase separation is also promoted by the increase in the molecular weight of the blocks and by the tendency of the rigid block to crystallise.

Despite the large number of methods at the disposal of investigators (transmission and scanning electron microscopy, large- and low-angle X-ray scattering, reversed gas chromatography), which makes it possible to determine the shape and size of the domains, the distance between them, and the nature of the interfaces, only certain classes of polyorgano-polysiloxane block copolymers have been investigated in detail owing to the difficulty of interpreting the results.

The composition and method of preparation of the specimen influences decisively the supermolecular structure of the block copolymer.

The studies of the supermolecular structures of polyorgano-polysiloxanes containing rigid amorphous blocks, comprising polycarbonate-polysiloxanes,[91-97] polyarylate-polysiloxanes,[98,102] polystyrene- and poly-α-methyl styrene-polysiloxanes[82,103,104] polyimide-polysiloxanes,[105] and polyamide-polysiloxanes[105] made it possible to put forward a morphological model of the block copolymer (Fig.2) in which certain rigid blocks are associated into domains, which act as a physical network, while the matrix consists of polysiloxane blocks, whereupon there is a possibility of partial interpenetration of the phases. When their content is low, the rigid blocks form a discrete phase, for intermediate contents both components form part of the continuous phase, and, for a high content of the rigid blocks, the polydimethylsiloxane aggregates into a discrete phase.

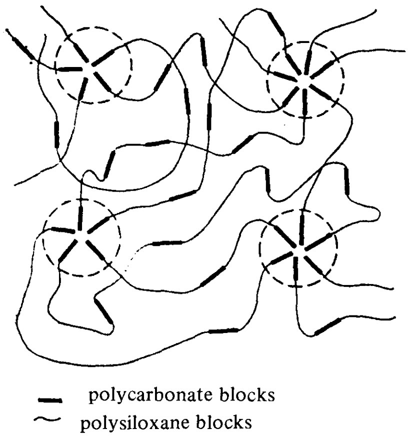


Figure 2. A morphological model of an amorphous polycarbonate–polysiloxane block copolymer.[91]

Depending on the composiiton of the block copolymer, the conditions in the preparation of the specimen, and the chemical nature of the organic blocks, the size of the domains formed by the latter varies over the range 30–350 Å.

The domains formed by the rigid blocks are separated by a distance of approximately 300 Å and the number of blocks in the domain may reach 800. With decrease in the molecular weight of the organic block, the presence of the mixed phase is manifested to a greater extent and the content of the polydimethylsiloxane component within the rigid domains increases. It has been noted that polycarbonate domains can contain up to 11 wt.% of the polydimethylsiloxane blocks.[95]

The statistically alternating block copolymers in which both blocks are polydisperse have a less ordered morphology than the block copolymers with a regular alternation of fragments. It has been suggested[94] that, in the formation of domains in such copolymers, long blocks are initially aggregated and small blocks are aggregated on the latter, which function as seeds. For this reason the short blocks "draw" the flexible polydimethylsiloxane blocks into the interior of the domain in the course of the formation of the structure.

When the content of the organic or the organosilicon blocks in the copolymer changes, the sizes of the domains can alter. Thus the surface area of the polycarbonate domains can be calculated from reverse gas chromatographic data,[96,97] and it has been shown that the area of the domains diminishes significantly with increase in the fraction of the carbonate block. The authors attribute this to the transition from the structure containing many small dispersed spherulites with a large surface area to a structure with close-packed folded domains.

A change in the method of preparation of the specimen for the same composition of the block copolymer results in a significant alteration of its structure. The supermolecular structure of film specimens then depends on the type of solvent and reflects the nature of the molecular associated species in solution. It has been shown[103,106,107] that, even in solutions of polyorganopolysiloxanes in selective and sometimes also in general solvents, the appearance of supermolecular formations and of a network between the domains has been observed, the microphase separation becoming more pronounced with increase of solvent selectivity. The most sensitive structural parameters under these conditions are the dimensions of the particles and the distance between them. For example, for polyarylate-polysiloxanes, increased selectivity of the solvent with respect to polydimethylsiloxane (enrichment of the solution in hexane) leads to a decrease in both the size of the domains themselves and in the distance between them. An analogous decrease of the distance between the domains occurs also for other methods of increasing the solvent selectivity and of altering the previous history of the specimen.

When the film is obtained from a solution in chloroform in an atmosphere of saturated xylene vapour with a gradual change in solvent composition as the xylene condenses and the chloroform evaporates, the distance between the domains decreases from 215 to 165 Å.[100]

Films based on polystyrene-polysiloxanes, obtained from toluene (common solvent), have a structure in which the polystyrene blocks produce agglomerates in the form of spaghetti-like microphases 282 ± 15 Å in diameter. The polydimethylsiloxane blocks give rise to a continuous matrix in which the polystyrene formations are separated by a distance of 170 ± 20 Å and the interpenetration of the phases is observed. With increase in the content of the polystyrene blocks, the agglomerates form cylindrical domains and there is a possibility of phase inversion.

Phase inversion has been achieved by choosing selective solvents for the same composition of the block copolymer. The toluene–cyclohexane (solvent for polydimethylsiloxane) mixture "displaces" polystyrene first on evaporation of the solvent, while films containing a discrete polydimethylsiloxane phase have been obtained from a toluene–bromobenzene (solvent for polystyrene) mixture.[103] Heat treatment of both blocks in the vicinity of the glass point promotes a better phase separation of the domain structures.[104]

Whereas the amorphous copolymers examined above exhibit some compatibility of the flexible and rigid blocks in both the continuous and discrete phases, the ability of the rigid blocks to crystallise leads to phase separation with a distinct interface.

Morphological studies of polysilphenylene-polysiloxanes revealed a two-phase structure, with a discrete phase comprising the crystallised silarylene block and an amorphous phase, consisting of non-crystallised polysilarylene and polydimethylsiloxane blocks, which is fully excluded from the crystal lattice regardless of the content of this phase in the copolymer.[108,109] The morphological model of the copolymer consists of lamellae alternating with the less ordered amorphous phase (Fig.3).

The degree of crystallinity depends on the amount of the polydimethylsiloxane component and diminishes from 53 to 15% with increase of the content of polydimethylsiloxane from 10 to 70 wt.%.[110] The temperature at which the maximum rate of growth of the crystals is observed diminishes with decrease in the content of the polysilarylene block.[111]

The morphology and cohesion between the phases in the block copolymer is influenced significantly by the solvent, temperature, conditions, and the time of formation of the structure.[112]

Thus the degree of microphase separation of polyorganopolysiloxane block copolymers is determined mainly by the composition of the copolymer, the method of preparation of the specimen, and also by the capacity of the rigid block for crystallisation.

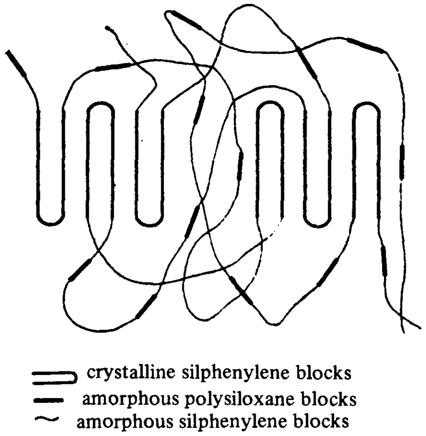


Figure 3. A morphological model of a crystalline polysilphenylene-polysiloxane block copolymer.[110]

2. The Temperature Dependent Transitions in Polyorganopolysiloxane Block Copolymers

The most characteristic feature of polyorgano-polysiloxanes, which follows from their ability to form morphological structures discussed above, is manifested by the presence of two glass points, reflecting the individual properties of each block (Table 3). Microlayer formation and the appearance of two glass points caused by it are observed for polyorganopolysiloxanes, starting with relatively low (3000–5000) molecular weights of the rigid block, which has been attributed to the large difference between the solubility parameters of the organic and polydimethylsiloxane blocks.

Table 3. Transition temperatures of polyorgano-polysiloxanes.

Organic block	T_c, °C	Transition temperatures of the block copolymer, °C			Refs.
		T_c	T_{g1}	T_{g2}	
Polysulphone	+160	−55	−110÷−120	+140÷+160	[11 113]
Polycarbonate	+149	—	−110	+37÷+104	[114]
Polycarbonate-urethane	—	−53÷−66	−105÷−110	+36÷+70	[58]
Polyarylate	+320	−50	−110÷−120	+320	[24.100]
Polystyrene	+88	−40÷−45	−108	+83	[81]
Poly-α-methylstyrene	+130	−45	−105÷−120	+80÷+130	[25]

The majority of investigators claim (Table 3) that the temperature dependent transition, which is attributed to glass formation by the polydimethylsiloxane block (T_{g1}) occurs at lower temperatures (−105 to −120 °C) and is almost independent of the molecular weights of the polydimethylsiloxane and organic blocks for all the block copolymers considered (Fig.4). Its temperature is close to the glass point of polydimethylsiloxane rubber (−120 °C).

The independence of T_{g1} of the molecular weight of polydimethylsiloxane for comparatively short lengths of the blocks (2000–3000) is probably associated with the appreciable flexibility of the polydimethylsiloxane chain and hence with the small length of the kinetic segments responsible for the glass forming processes.

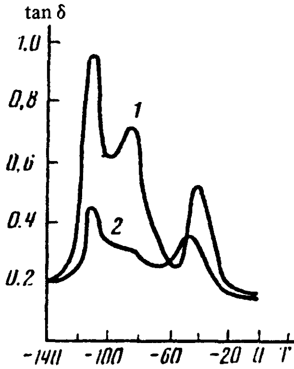


Figure 4. Temperature variation of the tangent of the mechanical loss angle (tan δ) for polyarylate-polysiloxane specimens having different compositions $N_{Si}:N_{Ar}$: 1) 420 : 20; 2) 200 : 20; N_{Si} = number of siloxane units and N_{Ar} = number of arylate units.[24]

However, a sharp increase[89,115] or decrease[116] of T_{g1} in polyorganopolysiloxanes compared with homopolyorganosiloxane has been noted in certain investigations. The authors were unable to give an unambiguous explanation, suggesting that such anomaly may be associated both with the change in the character of the packing of organosiloxane blocks and with the high degree of interpenetration of the phases during their segregation.

An increase of T_{g2} (the temperature dependent transition associated with glass formation in the rigid block) increases both with increase in the molecular weight of this block and with increase in the length of the polydimethylsiloxane block for constant lengths of the rigid block, which has been explained[25] by the increasing degree of phase separation. However, in polyarylate-polysiloxane[99] and polystyrene-polysiloxane,[82] T_{g2} hardly differs from the glass point T_g of the homopolymer over the entire range of compositions of the block copolymers investigated. The results obtained indicate, according to the authors, a more complete phase separation in these copolymers.

X-Ray diffraction studies have shown that the domains formed by silphenylene units have a high degree of crystallinity and the changes associated with glass formation by the rigid block are therefore very slight in these copolymers.[117]

Studies of polyarylene-polysiloxanes by differential scanning calorimetry also showed that there is a melting point of the silarylene blocks. With increase in the number of silarylene-siloxane units, the melting point increases and the decreased content of siloxane units also causes an increase in the melting point of the silarylene-siloxane domains.[115,118]

The decreased melting points of the silarylenesiloxane and polydimethylsiloxane blocks compared with the melting points of the corresponding homopolymers can probably be accounted for by the fact that, although the structures of the crystal lattices of the domains of the homopolymers and the block copolymers are identical (their X-ray diffraction parameters are the same), the lattices of the domains in the block copolymers are more defective,[117,119] since the development of crystallisation processes is limited by the incomplete segregation of the individual sections of the macromolecules to form domains.

It is of interest to note that amorphous polyorgano-polysiloxanes, for example, polycarbonate-polysiloxanes,[120] can be crystallised by being kept in the vapours of chlorinated hydrocarbons. The degree of crystallinity determined by the crystallisation of the polycarbonate component of the block copolymer diminishes with increase in the content of the siloxane component in the copolymer. The maximum attainable degree of crystallinity (up to 45%) for block copolymers with any silicon content is higher the greater the length of the siloxane fragment.

The crystallisation of systems containing high-molecular-weight polydimethylsiloxane blocks has been noted at a temperature T_c. The degree of crystallinity depends little on the length of the rigid block and is close to the degree of crystallinity of the pure polydimethylsiloxane rubber.[121]

The temperature dependent transitions are an important characteristic of block copolymers, since they in fact determine the temperature ranges within which these materials can be worked and used.

3. Deformation-strength Properties

The mechanical characteristics of elastoplastics are determined by the properties of the continuous phase and by the frequency of the physical cross links and they therefore depend on the same factors as the supermolecular structure: the composition of the copolymer and the method of preparation of the specimen.

Table 4. The deformation-strength properties of polyorgano-polysiloxane block copolymers.

Organic block	c, wt.%	σ, MPa	ε, %	E, MPa	Refs.
Polysulphone	55	17	350	140	[11]
Poly(phenylene oxide)	49	18	450	—	[17]
Polycarbonate	51	21	150	—	[114]
Polycarbonate-urethane	56	25	500	—	[58]
Polyarylate	60	15	180	—	[90]
Polysilarylene	50	13	750	10^3—10^4	[111,118]
Poly-α-methylstyrene	52	13	370	500	[25]

Notation: c is the content of the polydimethylsiloxane blocks, σ the breaking tensile stress, ε the relative elongation on rupture, and E the modulus of elasticity.

The main characteristic of the mechanical properties of the copolymers is the relation between the breaking tensile stress and the relative elongation on rupture. This relation determines the modulus of elasticity of the system, its strength, and its deformability.

With increased content of the polydimethylsiloxane component, the properties of all the polyorgano-polysiloxane block copolymers vary from those of rigid materials, which are difficult to deform, to flexible elastomeric compositions, which is well illustrated by Fig.5 for polycarbonate-urethane-polysiloxanes.[58]

The different conditions in the preparation of the specimens and in the tests preclude quantitative estimation of the influence of the chemical structure of the rigid block on the deformation-strength properties of the copolymer. However one may note that the presence in the block copolymer of fragments with an increased tendency towards crystallisation [poly(phenylene oxide), polysilarylene] or capable of forming interchain hydrogen bonds (polycarbonate-urethane) increases its deformability (Table 4).

It is essential to note that the molecular weight of the block copolymer has an appreciable influence on its deformation-strength properties (Fig.5).

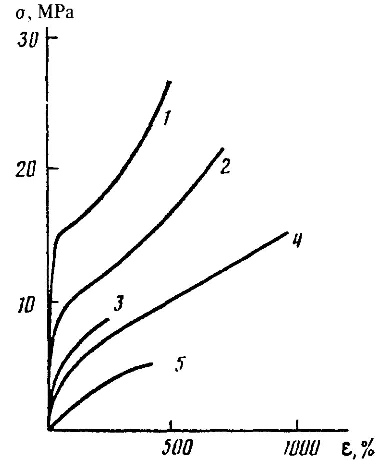


Figure 5. The influence of the composition and molecular weight of polycarbonate-urethane-polysiloxanes on the breaking tensile stress σ and the relative elongation on rupture ε; content of polydimethylsiloxane blocks (wt.%); 1) 56; 2) 62; 3) and 4) 67; 5) 77; $\bar{M}_w$: 3) 5×10^4; 4) 11×10^4.[58]

The deformation-strength properties of films based on a block copolymer of one composition can be varied within wide limits by altering the method of their preparation. On passing from a common to a selective solvent, the properties of the film approach those of the component with respect to which the solvent is selective, which is associated with the different character of structure formation in the solution from which the film is obtained.[115,122,123]

It has been shown in relation to polyarylate-polysiloxane[122] that the change in strength is manifested to a greater extent in systems enriched in the rigid block (the polyarylate) and the change in deformability is manifested more in systems enriched in polydimethylsiloxane. The influence of the solvent and of the method of formation of the film is particularly marked in systems with similar weight fractions of the components.

The expansion of the region of high elasticity occurs, as can be seen from Table 5, when the film is obtained via a gel stage, compared with the film obtained from the same solvent via the solution stage or after swelling the film in a medium in which it forms a gel and is then dried.[100]

A distinctive feature of almost all polyorgano-polysiloxane block copolymers is their ability to be worked in the melt at temperatures above the glass point of the rigid blocks. In thermal moulding, the material is usually oriented, which leads to an appreciable increase of strength.[124]

Table 5. Dependence of the deformation-strength properties of a polyarylate-polysiloxane on the nature of the solvent and the method of preparation of the film.[100]

Solvent	Solvent selectivity	σ, MPa	ε, %	E, MPa
Chloroform	common	13.0	160	66.0
Tetrachloroethane	polyarylate	19.0	95	100.0
Xylene	polydimethylsiloxane	3.0	220	7.5
Chloroform-hexane (60-40)	»	9.5	280	10.0
Chloroform-toluene (70-30)	»	9.0	420	29.0
Chloroform-hexane (60-40*)	»	10.5	375	—
Xylene (from the gel)	»	9.5	270	—

*Film obtained from solution in chloroform, swollen in a chloroform–hexane mixture, and dried.

4. Thermal and Thermo-oxidative Stability

The thermal and thermo-oxidative degradation of polyorgano-polysiloxanes has been investigated to determine the temperature and conditions for their processing and to estimate the possibility of using these materials at elevated temperatures.[11,27,63,125–127] In the first place, it is essential to note that the high energy and ionic character of the siloxane bond are responsible for the appreciable thermal stability of polysiloxane. The Si–O–C bond is more vulnerable in this respect.[128] Since the rigid blocks of the copolymers investigated also exhibit a high thermal stability, it follows that, as was to be expected, the block copolymers are stable up to high temperatures (Table 6).

Table 6. Thermal stability of polyorgano-polysiloxanes.

Organic block	Temperature of 10% weight loss, °C		Refs.
	in air	in nitrogen atmosphere	
Polysulphone	475	510	[11]
Polycarbonate	400	450	[127]
Polycarbonate-urethane	350—400	—	[58]
Polyarylene	420	480	[11]
Polysilarylene	—	427	[129]
Polyimide	—	500	[66]

As a rule, the weight content of the blocks in the copolymer changes and no appreciable alteration of the thermal stability is observed.[127,129] The reason for this is probably that the stability of the macromolecule is determined by its weakest bonds, which are located at the sites of contact between the blocks (the Si–C or Si–O–C bonds). Polyarylene-polysiloxanes, whose thermal degradation takes place preferentially with rupture of the Si–O–Si linkage whereupon the thermal stability of the copolymer diminishes with increasing content of the polysiloxane block,[130] and polysulphone-polydimethylsiloxane copolymers where the polydimethylsiloxane blocks are the first to undergo thermal degradation with formation of linear and cyclic oligodimethylsiloxanes,[131] are exceptions.

The change in the chemical structure of the rigid block (within the framework of a single class) is reflected in the thermal stability of the block copolymer.[80,129,132,133] The poly-α-methylstyrene-polysiloxane block copolymers, for example, exhibit a better thermo-oxidative stability than polystyrene-polysiloxanes having the same composition.[80] Whereas heating of polystyrene-polysiloxane in air for 80 h at 150 °C diminishes its strength by a factor of 2, this is not observed for poly-α-methylstyrene-polysiloxane.

The study of the time variation of the weight losses at 305–385 °C by polyarylate-polysiloxanes based on phenolphthalein and phenolfluorene terephthalates[133] showed that the thermal stability of the latter copolymer is higher; this has been attributed to the absence from it of the thermally unstable lactone group. As has been frequently noted,[129,134] copolymers without Si–O–C bonds in the main chain show a higher thermal stability.

5. Hydrolytic Stability

The resistance of polyorgano-polysiloxane block copolymers to hydrolysis is one of the principal indices indicating the retention of the properties of polymeric articles under the real conditions of their use. The hydrolytic stability of polyorgano-polysiloxanes is lower than that of homopolymeric polysiloxane and the degradation of the polymer takes place as a rule at the bonds between the organic and organosilicon blocks or within the organic block.

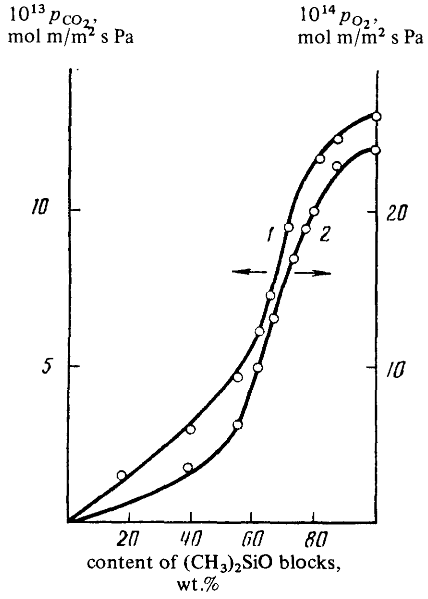


Figure 6. Dependence of the coefficient of gas permeability to CO_2 (P_{CO_2}) (curve *1*) and O_2 (P_{O_2}) (curve *2*) on the composition of polycarbonate-polysiloxane at 20 °C.[114]

It has been shown[135] that the heterogeneous hydrolytic degradation of polyarylate-polysiloxane in argon takes place to an appreciable extent at 160 °C, while the hydrolysis of polydimethylsiloxane under analogous conditions does not begin until 220 °C. It has been noted that the hydrolysis proceeds preferentially at the Si–O–C linkage and that the rate of hydrolysis increases with increase in its concentration per unit volume.

The stability of polysulphone-polysiloxanes containing the Si–O–C bond can be increased by introducing large hydrophobic silicon-containing segments into the main chain of the macromolecule.[136] As a result of this, steric hindrance arises in the hydrolysis of the Si–O–C bond and the concentration of such bonds in the copolymer falls. The hydrolytic stability of polyorganopolysiloxanes can be raised also by introducing polyester-urethane[76] fragments into the siloxane chain.

An increase in the hydrolytic stability of the block copolymers can be achieved by replacing the hydrolytically vulnerable Si–O–C bond between the blocks by the Si–C bond.[58,63,66,137]

Estimation of the hydrolytic stabilities of various polysiloxanes showed[138] that the replacement of the methyl groups in polydimethylsiloxane by sterically more bulky substituents (phenyl, ethyl, and trifluoropropyl groups) increases the hydrolytic stability of homo- and co-polysiloxanes. One can therefore assume that the synthesis of block copolymers from such polysiloxanes would make it possible to increase their hydrolytic stability.

6. The Resistance of Polyorgano-polysiloxanes to UV Radiation

In connection with the possibility of using organosiloxane block copolymers as transparent materials without a filler such as carbon black, studies have been made of the resistance of these polymers to UV radiation. The block copolymers of polyorganosiloxane and polystyrene showed satisfactory photostability.[139] However, the stability of copolymers containing aromatic rings in the main chain proved to be limited.[11,140]

The study of the photodegradation of polyarylate-polysiloxane showed that the degradation takes place mainly in the polyarylate block and that the most unstable structures in relation to UV radiation are the ester bond and the phthalide ring. The siloxane block does not absorb UV radiation but does undergo degradation with evolution of methane, which has been attributed to the occurrence of secondary radical reactions.[140] The presence of oxygen appreciably accelerates the degradative processes.

7. The Permeability of Polyorgano-polysiloxanes to Gases

Polyorganosiloxanes are known[141] to be distinguished by a high permeability to gases owing to the high flexibility and mobility of the Si–O–Si bonds and also to the weak intermolecular interaction between such macromolecules.

An advantage of the two-phase polyorgano-polysiloxane block copolymers is that strong thin film membranes can be obtained from them without chemical cross-linking or the use of a filler. The presence of the highly permeable siloxane block therefore entails prospects for an important application of the block copolymers considered as gas separating membranes.

The permeability of such membranes to gases is up to 80% of the permeability of siloxane rubber and increases with increasing content of the polydimethylsiloxane blocks in polyarylate-polysiloxanes,[63,142] polycarbonate-polysiloxanes,[114] polycarbonate-urethane-polysiloxanes,[58] and polysulphone-polysiloxanes.[143]

The study of the influence of the composition of polycarbonate-polysiloxane on the gas-permeability to CO_2 and O_2, carried out by the gas-chromatographic method on film specimens,[114] revealed the S-shaped character of the dependence of the gas-permeability coefficient on the content of the polydimethylsiloxane blocks (Fig.6). The sharp increase in this coefficient in the region where the content of the polydimethylsiloxane blocks is up to 50–60 wt.% suggests that phase inversion takes place for this composition of the copolymer.[114]

The selectivity of the gas separation (CO_2/O_2) remains approximately 6 regardless of the composition of the copolymer. This has been attributed[114] to the fact that the properties of the siloxane phase depend little on the composition of the copolymer. It has also been noted that a characteristic feature of the membranes in the region of compositions investigated is the virtual absence of a temperature dependence of the permeability to CO_2 in the range 20–90 °C as a function of the ratio of the block lengths. This has been explained by the mutual compensation of the activation energies for the diffusion of CO_2 and the heat of solution of CO_2 in the block copolymer.

Since the permeability to gases is determined by the content of the siloxane component regardless of the nature of the rigid blocks constituting the relatively impermeable phase, comparison of the block copolymers having different organic blocks[144] showed that they are to a large extent analogous in their gas separating properties. For this reason, in selecting polymeric materials for gas separating membranes, the criterion to be used as a guide should probably be their physicochemical characteristics, their resistance to degradation, and the technological feasibility of their preparation.

Analysis of the literature data permits comparative estimation of the properties of polyorgano-polysiloxane block copolymers containing different rigid elements (Table 7).

Table 7. Comparative characteristics of the properties of polyorgano-polysiloxane block copolymers*.

Rigid block	Deformability	Upper temperature limit of operating range	Thermal stability	Hydrolytic stability	UV stability	Mouldability	Thermoweldability	Atmospheric stability
Polysulphone	*	*	+	+	*	—	—	—
Poly(phenylene oxide)	+	+	—	*	*	—	—	—
Polycarbonate	*	*	*	*	*	*	+	*
Polyarylate	*	+	+	*	*	*	—	*
Polysilarylene	+	+	*	*	*	—	—	*
Polystyrene	*	—	*	*	+	+	—	+
Poly-α-methylstyrene	*	—	*	*	—	+	—	—
Polyurethane	+	*	*	+	—	*	—	*

Notation: "*"—presence of given property; "–"—absence of given property (or information about it); "+"—advantage in terms of the given property.

The Table shows that such block copolymers have a set of useful properties. The choice of the material for each specific application is determined by the property which should predominate.

It is noteworthy that, since modern economic trends are characterised by a tendency towards further growth of prices of petrochemical raw materials and energy, the manufacture of organosilicon products and materials based on them will be one of the most promising branches of chemical industry due to the relatively low consumption of raw materials and energy per unit output.[145]

IV. APPLICATIONS

Polyorgano-polysiloxane block copolymers can be used for the modification of homopolymers whose structure is analogous to that of the rigid fragment. Small amounts of added block copolymer (approximately 5%) impart new and unexpected properties to the homopolymer. The possibility of such modification follows from the two-phase morphology and the specific properties of the polyorganosiloxane block.

Thus the introduction of 5 wt.% of polysulphone-polysiloxane into the polysulphone homopolymer increases its impact strength by a factor of 20; this is also accompanied by an increase in the resistance to cracking.[9,126] Such behaviour can be explained by the solubility of the polysulphone fragment of the block copolymer in the chemically identical homopolymer matrix and by the segregation of the polysiloxane blocks into a discrete phase. This leads to the effective dispersion of the copolymer in the matrix and a high degree of interfacial adhesion.

A characteristic feature is that the modification is observed only after the introduction of a copolymer exhibiting a two-phase morphology.[14] The increased deformation following the rupture of polycarbonate-(polycarbonate-siloxane-urethane) blends compared with the deformations of the two components of the blend can be accounted for by analogous causes.[146]

Another possible type of modification involves the decrease in the wettability and of the coefficient of friction of the surface of the homopolymer by introducing into the latter a certain amount of the block copolymer.[63,147]

It has been shown by X-ray photoelectron microscopy[148,149] and electronic spectroscopy for chemical analysis[150] that the surface of the block copolymer and of the homopolymer–block copolymer blend is always enriched in the component with the lower surface energy, i.e. in the polysiloxane,[151] which ensures the modifying effect.

The principal applications of polyorgano-polysiloxane block copolymers are determined by the ability of these copolymers to effect highly productive selective separation of gases.[152]

Films based on polyarylate-polysiloxane are used as membranes for the enrichment of natural gas in helium[153] and for the isolation of helium from petroleum gas,[154] for the separation of the "carbon dioxide–hydrogen" or "oxygen–nitrogen" gas mixtures,[62,137,144,155] and for the isolation of sulphur dioxide from mixtures.[156] Polycarbonate-polysiloxane is used for the isolation of oxygen from "nitrogen–oxygen" mixtures.[157,158] Gas- and water-permeable coatings are obtained from polystyrene-polysiloxane.[159]

Ultrathin membranes,[160,161] thermostable films,[162] and films with thermal shrinking for the packing of food products[15] can be obtained by processing polysiloxane block copolymers. These materials are suitable for coatings with improved dielectric properties[66,163,164] and for non-shrinkable coatings with improved strength characteristics.[165] These coatings adhere to metallic surfaces,[166] exhibit a satisfactory resistance to the action of light and weather,[139] and, by virtue of their hydrophobic nature, prevent the icing of glass.[167]

The block copolymers of the given type are believed to be effective stabilisers of polymers[168] and are used as part of compositions with high impact strength,[169–172] thermal stability,[173] and effective adhesion properties[174] and as part of soil compositions.[175]

Polyorgano-polysiloxane block copolymers exhibit a satisfactory fire resistance,[176–179] which increases with increasing content of the siloxane blocks. This has been explained by the formation during combustion of varieties of coke-containing silicon, which increases the resistance of the material to oxidation.[180] Depending on the chemical structure of the organic fragment, the first resistance increases in the sequence polycarbonate based on di(hydroxyphenyl)propane = polycarbonate based on di(hydroxyphenyl)fluorene > polystyrene-poly(2,6-diphenyl-1,4-phenylene oxide).[181]

These materials have found applications in electrical engineering[182] as electrically insulating materials and in electronics[183,184] as coatings for transistors, resistors, and integrated circuits. They retain their useful properties at both elevated[185] and reduced[186] temperatures.

Laminated materials, in which the inner adhesive layer is a polycarbonate-polysiloxane,[29,187,188] as well as technical filaments made of polymethylstyrene-polysiloxanes[189] have been described.

A promising field in which polysiloxane block copolymers may be used currently is medicine.[190,191] Among all the synthetic polymers used in medicine in the USSR, organosilicon compounds are the commonest.[192] All the siloxane elastomers are used as vulcanised materials, reinforced by a filler, which are readily sterilised. However, their main disadvantage, which significantly restricts their applications, is their low mechanical strength and low anticlotting activity.

It is striking that the anticlotting properties of filled silicone rubber are determined not by the chemical nature of the rubber but by the presence on its surface of a filler—silicon dioxide, whose silanol groups are capable of forming hydrogen bonds with plasma proteins and inducing the coagulation of blood.[76,193] The use of polyorgano-polysiloxane block copolymers for medical purposes permits the elimination of these disadvantages. It was shown above that their strength can vary within wide limits and can surpass the strength of siloxane rubber by a factor of 2–3.

The copolymer containing 90 wt.% of polyester-urethane and 10 wt.% of polydimethylsiloxane is used nowadays as a blood-compatible material, having the necessary set of formation-strength characteristics.[76,150,194] Auxiliary devices for the maintenance of cardiac activity, intra-aortal balloons, and various types of pumps for ensuring the circulation of blood and made from this material.

Polyorgano-polysiloxane block copolymers are used as biomaterials,[73,77] medical hermetic sealing compounds,[195] and optical contact lenses correcting astigmatism.[196]

The possibility of obtaining selective gas-permeable films from copolymeric materials permitted their use as the membrane element in different types of "artificial lung" apparatus.[190]

The polyorgano-polysiloxane block copolymers examined in this review represent a new class of materials with a set of useful practical properties determined by their microheterogeneity. Detailed investigation of the factors permitting a fine regulation of the supermolecular structure of these copolymers will assist in the creation of materials with properties specified beforehand.

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During the preparation of this review for printing, new communications concerning research into polyorgano-polysiloxanes were published.

The synthesis of linear soluble block copolymers based on αω-diepoxyoligosiloxanes and the diglycidyl ether of di(hydroxyphenyl)propane at 60 °C in dioxan in the presence of stoichiometric amounts of piperazine has been examined.[197]

The interaction of diepoxy-derivatives of oligosiloxane with $\alpha\omega$-di(hydroxyphenyl)oligosulphones in concentrated solution at elevated temperatures resulted in the formation of polysulphone-polysiloxanes,[198] but the molecular weights of the block copolymers synthesised proved to be low.

A number of publications deal with questions of the synthesis and modification of polyamide-polysiloxanes,[199,201] polyurea-polysiloxanes,[202,203] and polyimide-polysiloxanes[204–207] with participation of $\alpha\omega$-diaminosiloxanes. High-molecular-weight polyamide-polysiloxanes have also been obtained by the copolymerisation in the melt at 130 °C of oligodimethylsiloxane having terminal anhydride groups with ε-caprolactam in the presence of an anionic initiator.[208]

The methods of synthesis of polyester- and polyurethane-polysiloxanes using organic functional group-substituted $\alpha\omega$-dihydroxy(carboxy)oligosiloxanes[202,203,209,210] and $\alpha\omega$-di(chloroformyloxymethyl)oligosiloxanes[211] and the hydrosilylation reaction[212,213] in the synthesis of polysulphone-polysiloxanes are being developed.

The detailed study of the physicochemical properties of polyorganopolysiloxanes is being continued. The composition and structure of block copolymers,[214,215] their microheterogeneity characteristics,[216–222] their surfaces,[223,224] the molecular mobility at the interface,[225] processes involving the transport of gases across membranes made of such block copolymers,[226,227] their biodegradation,[228] and their operating properties[229] have been analysed by different methods in recently published studies.

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Kinetic Aspects of the Irreversible Thermal Inactivation of Enzymes

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The methods for the kinetic description and the mechanisms of the thermal inactivation of proteins (enzymes) in various media (aqueous solutions, inverted surfactant micelles, and microsomal membranes) are examined critically. The effective kinetic constants calculated from a first order equation and by approximate methods in conformity with an associative-dissociative mechanism are compared. The temperature dependence of the effective inactivation rate constants is analysed for enzymes and the causes of its deviation from the Arrhenius equation are discussed. The influence of polyols and detergents on the stability of enzymes and their modified forms is analysed and the thermodynamic activation parameters (ΔH^*, ΔS^*, and ΔG^*) for the thermal inactivation of different enzymes in various media are compared and discussed. Recommendations are given concerning the quantitative description of the thermal stability of proteins (enzymes) under the real conditions of their application.

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I. INTRODUCTION

Major advances have now been achieved in the study of the structure and the principles governing the structural organisation of proteins,[1] but the problem of establishing the interrelation between the structure and stability of biomacromolecules remains one of the unsolved problems in modern biophysical chemistry.[2] It is well known that the changes in the conformation of proteins affect their spectroscopic and many other physicochemical characteristics.[1-3] Sometimes these characteristics fail to "notice" small and only at first sight insignificant conformational transformations of proteins. Slight changes in the structure of the active centre of the biomacromolecule fairly frequently have a significant influence on its stability and functional activity. The study of the loss of stability and activity by proteins is of fundamental importance for modern enzymology, bioorganic chemistry, and related disciplines. On the other hand, unless the principal structural factors determining the stability of protein molecules in media of different nature are known, it is impossible to solve practical problems concerning the stabilisation of biologically important polymers. The necessity for the solution of this problem is dictated by the development of modern biotechnology and engineering enzymology, which require the carrying out of many enzymic processes under severe conditions, i.e. at elevated temperatures, under the influence of mixtures of organic solvents, in aqueous media with extreme pH values, in the presence of detergents of different nature, etc.

Modern biotechnology requires accurate quantitative characteristics of the stability of biopolymers. Numerous data obtained under different conditions frequently cannot be compared let alone used in calculations for enzyme reactors, the permitted usage times of biopreparations, etc. because of the lack of a quantitative treatment. The quantitative characteristics of the stability of biopolymers are especially important under the conditions of their practical application, i.e. in aqueous media, in the presence of organic solvents, detergents, denaturing additives, and stabilising substances, and in the immobilised state.

The interest in the inactivation and reactivation of proteins and enzymes was manifested very long ago[4,5] and this multiaspect problem still remains in the centre of attention of specialists in various disciplines.[3,6–23] Various aspects of the denaturation and inactivation of biopolymers have been examined in monographs,[3,7–11,14,16,18] review articles,[12,13,15,17,21,22] and textbooks.[1,2] The structure of proteins and the role of conformational changes in their denaturation processes have been described in detail in several books.[1–3,9–11] The thermodynamics of the reversible and irreversible denaturation processes have been considered in a number of communications.[3,7,12] The methods for the investigation of the denaturation processes involving proteins and enzymes have been described in detail in the books by Joly[3] and Kushner.[11] The biological aspects of the stability of multienzyme complexes and other biopolymers have been dealt with by Kushner and the kinetic aspects of this problem have been considered in the monograph of Berezin and Varfolomeev.[16] The principal ways of stabilising enzymes have been examined in a number of communications[13–15,19,22] and two reviews[20,21] have been devoted to problems of the reactivation of biocatalysts. The general characteristics of the changes in the thermal stability of proteins and enzymes after the chemical modification of their functional groups have been considered in a review[22] and the relative contributions of thermodynamic and kinetic factors to the stabilisation of immobilised proteins have been dealt with by Kozlov.[23]

In our view, the extensive but by no means complete literature data mentioned above reflect inadequately and sometimes do not deal with many important kinetic aspects of the irreversible inactivation of enzymes. Regarding the stability of enzymes as a function of their structure, which in many respects depends on the environment, and being guided by the fundamental and practical problems mentioned above, we had several specific aims in the present review: (1) to examine the methods for the rapid and correct characterisation of the rates of enzyme inactivation processes under the real conditions of the application of enzymes; (2) to characterise quantitatively the thermal stability of a number of enzymes (lysozyme, lactate, malate, and glucose-6-phosphate dehydrogenases, horseradish peroxidase, and catalase) and proteins (myoglobin and cytochrome b_5) by means of these procedures; (3) to compare in relation to specific examples the thermal stabilities of enzymes in aqueous solutions and inverted surfactant micelles in organic solvents (peroxidase, glucose-6-phosphate dehydrogenase, and cytochromes b_5 and P-450) and also in aqueous solutions and in native biological membranes (cytochrome P-450); (4) to analyse the characteristic features of the stabilising action on enzymes by polyols and detergents of different nature; (5) to consider critically the thermodynamic activation characteristics of the irreversible inactivation of proteins under various conditions and the possibility of their relation with the structure of the biopolymers and the environment.

II. METHODS FOR THE KINETIC CHARACTERISATION OF THE INACTIVATION OF PROTEINS

The concept of "inactivation" is frequently incorrectly replaced in the literature by the term "denaturation". Inactivation is always associated with the loss of functional activity by the protein and enzyme and can be due to a series of causes which do not induce the denaturation of the biopolymer. The term "inactivation" is much broader than "denaturation". We shall attempt to define clearly these concepts. Kushner has analysed the different definitions of the denaturation of biopolymers.[11] As a result, he justified what he believed to be the most correct definition of this process, namely that denaturation is a conformational change in the biological macromolecule leading to the irreversible or reversible loss of its ability to perform a specific biological function. Denaturation can be induced by physical and chemical factors (heating, ultrasound, irradiation, extreme pH values) and may accompany protein aggregation processes, the dissociation of the subunit biomacromolecules into monomers, the thiol–disulphide exchange, and the cleavage of S–S bonds and can also be the result of immobilisation and chemical modification of the functional groups of the biopolymer.[3,11,20–23] It is assumed that the denaturation process is not accompanied by the dissociation of covalent bonds in the polymer chains of the biomacromolecule.[1–3,11,13,14] The denaturation of the protein always leads to its inactivation. However, inactivation may be caused by factors which do not entail conformational consequences, i.e. denaturing: for example, the interaction of macromolecules with one another or the modification of functionally important groups which does not alter the conformation of the biopolymer as a whole.[20,21] Thus any change leading to the irreversible or reversible loss of a specific biological function may be regarded as the inactivation of the biomacromolecule.

The reversible "native protein (nat) $\rightleftarrows$ inactivated protein (in)" process can be characterised by the equilibrium constant K = [in]/[nat], where [in] and [nat] are the equilibrium concentrations of the inactivated and native forms respectively. In this case, if the protein is present in a highly dilute solution, the equilibrium constant K can be related to the characteristics of the equilibrium inactivation (the enthalpy ΔH and entropy ΔS) by the expression:

$$-\ln K=\Delta G/RT=\Delta H/RT-\Delta S/R$$

The enthalpy ΔH can be determined from the van't Hoff equation subject to the condition that ΔH and ΔS are independent of temperature:

$$-[\mathrm{d}\ln K/\mathrm{d}(1/T)]=\Delta H/R$$

The values of ΔH and ΔS have now been measured by various methods for the reversible inactivation processes involving a multiplicity of proteins. In order to determine these thermodynamic characteristics, measurements are made of the equilibrium constant between the native and denatured forms or the heat of denaturation is found by scanning microcalorimetry.[12] Tables giving compilations of these data may be found in monographs and reviews.[1–3,7,10–12]

An experimental criterion in testing for irreversibility is especially important in the study of irreversible protein (enzyme) inactivation processes. Those proteins whose functional activity has changed in such a way that after the removal of the given influence the initial level of functional activity is not restored for a long time should be regarded as irreversibly inactivated.[20] A certain indefiniteness in this concept is associated with the arbitrary choice of the time after which the initial functional activity of the protein is not restored.

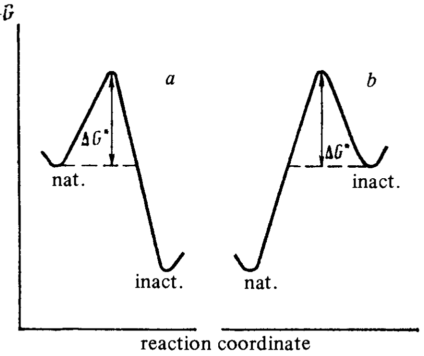

Figure 1. The energy diagram for the possible pathways in the irreversible protein inactivation process: *a*) thermodynamic; *b*) kinetic.[20,21]

The nature of irreversible inactivation can be both thermodynamic and kinetic (Fig.1).[20,21] In the former case the free energy of the stabilisation of the protein $\Delta G_{\mathrm{in}} = G_{\mathrm{in}} - G_{\mathrm{nat}}$ is greater than zero and the free energy of its destabilisation $\Delta G = -\Delta G_{\mathrm{in}} < 0$. The protein cannot be reactivated, since the free energy of the native form is characterised by a local minimum, while the free energy of the inactivated form is characterised by a global minimum (Fig.1*a*). In the case of the kinetic irreversibility, the protein passes from the native state with a global free energy minimum to the inactivated state with a local minimum in the Gibbs free energy: in this case the free energy of the stabilisation of the protein $\Delta G_{\mathrm{in}} < 0$ and the energy of its destabilisation $\Delta G = -\Delta G_{\mathrm{in}} > 0$. The two states are separated by a high activation barrier, which prevents the rapid reactivation of the protein (Fig.1*b*) The practical separation of thermodynamic and kinetic irreversibility in the inactivation of proteins is a complex problem, the ways for the solution of which are only being outlined.[23] The aim of the present review is not the analysis of the contributions to the thermodynamic parameters ΔG, ΔH, and ΔS by forces of different nature and the examination of data on the reversible inactivation of proteins, since this has already been done in a monograph[3] and other reviews.[12,17,22]

In irreversible inactivation, the kinetic stability of proteins has come to be characterised by the rate constant k_{in}, which is usually determined from the variation of the properties of proteins by fluorescence and electronic and circular dichroism (CD) spectroscopic methods or from the change in activity. In the general case, the retention of the activity of the biocatalyst does not always correspond to the retention of the integrity of the entire protein globule.[22] If one of the postulates of the theory of absolute reaction rates, stating that the rate of attainment of equilibrium between the reactants and the activated complex is much greater than the rate of the chemical reaction itself, is valid, then this theory can be applied to protein inactivation processes.[3,6] According to Eyring,[6] we have the following expression for molecular reactions:

$$k_{\text{in}}=(kT/h)\exp(-\Delta G^{*}/RT)=(kT/h)\,\mathrm{e}^{\Delta S^{*}/R}\mathrm{e}^{-\Delta H^{*}/RT}\ , \tag{1}$$

where k is the Boltzman constant, h the Planck constant, and ΔG^*, ΔH^*, and ΔS^* are the increments in the free energy, enthalpy, and entropy on formation of the activated complex. The change in the activation enthalpy is linked to the activation energy by the relation $\Delta H^* = E_{\text{act}}-RT$.

However, in the early studies, whose complete survey may be found in a monograph,[3] it was already shown that the irreversible inactivation process can be described by a kinetic first-order equation for by no means all enzymes and not under all conditions. The enzyme inactivation kinetics frequently do not obey the first order law from the beginning of the process or are not described by this law when the inactivation of proteins is continued until the attainment of high degrees of inactivation. The first order equation is usually inapplicable to the description of the inactivation of subunit enzymes in buffer solutions.[24–33] It has been shown[24–32] that, in the inactivation of alkaline phosphatase,[31] kidney acylase,[29] and glucose oxidase,[26,27] these subunit enzymes dissociate into the monomers, which are then irreversibly inactivated. The dissociation of the enzyme into subunits is observed also in the inactivation of glyceraldehyde-3-phosphate dehydrogenase,[34] catalase,[35,36] and many other proteins with a quaternary structure.[20,21,37–39] The appearance of subunits in the inactivation of enzymes has been confirmed by gel-electrophoretic[26,27,29,34] and sedimentation[36] methods. Numerous experimental data have shown that the inactivation of subunit enzymes can be described in the simplest case by the scheme:[24–33]

$$\mathrm{E}\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}\mathrm{A}\xrightarrow{k_2}\mathrm{I}\ , \tag{2}$$

where E is the native enzyme, A its reversibly denatured form which partly retains its catalytic activity or a subunit of the oligomeric enzyme, and I the irreversibly inactivated form of the protein lacking enzyme activity. For many enzymes, the inactivation scheme may be much more complex, since the process includes not one but several reversible stages, which greatly hinders its kinetic description. For example, in the presence of Mg^{2+} or Zn^{2+} ions, alkaline phosphatase forms tetramers, which are inactivated via a three-stage dissociative mechanism:[31]

$$\mathrm{E}_4 \rightleftarrows 2\mathrm{E}_2 \rightleftarrows 4\mathrm{E} \rightarrow 4\mathrm{I} \tag{3}$$

In scheme (3), the tetramers E_4 and the dimers E_2 are catalytically active, while the monomers E are inactive and the form I is irreversibly denatured. It has been stated that only the alkaline phosphatase dimers E_2 are catalytically active in the enzymic process.[40] The dissociative mechanism of the inactivation of many subunit proteins is not unexpected, since it reflects their complex structural organisation and the important role which structural levels of different orders play in the functioning of oligomeric protein.

At first sight, it is surprising that comparatively simple monomeric proteins, for example, lysozyme, exhibit a complex inactivation pattern both in solution and in the crystalline state: at pH 3–7 the thermal inactivation of lysozyme is a two-stage reversible process,[41] which corresponds to scheme (2). The stepwise character of the thermal denaturation of lysozyme has been confirmed by the change in the optical density of its solutions in the temperature range 20–90 °C. At 60–70 °C conformational changes take place in lysozyme in solution, accompanied by a decrease of the content of α-helices from 30 to ~10%. Conformational transitions in lysozyme in solution between 20° and 30 °C have been observed also by ^{13}C NMR.[43] The inactivation of lysozyme by ultrasound in the temperature range 20–80 °C showed that the enzyme undergoes several conformational transitions, including one which occurs at ~30 °C.[44] The study of the thermal denaturation of lysozyme in weakly alkaline solutions by fluorescence[45] and circular dichroism[46] methods confirmed the validity of scheme (2) for this enzyme. In the first irreversible stage of the inactivation of lysozyme, the α-helix structure of the protein changes little, but in the second, irreversible stage its complete breakdown is observed over section 5–15 of the polypeptide chain together with the ionisation of the Glu-35 residue, which greatly destabilises the adjoining α-helices. We obtained data indicating the maximum rate of inactivation of the protein in solution at pH 6.5, which confirmed the important role of Glu-35 in the irreversible inactivation of the enzyme,[47] since $\mathrm{p}K_a \cong 6.5$ which is characteristic of only the Glu-35 residue localised in the lysozyme molecule in the vicinity of the active centre.[48,49]

We have examined two causes of the deviation of the inactivation of enzymes from the kinetic first-order law—the subunit nature of many proteins and the complex multistage character of the inactivation of monomeric proteins. In a study of the inactivation of enzymes in biological membranes, the process kinetics are complicated still more by the involvement in the process of isoenzymes of the same enzyme or of different conformers of the same form of the protein. This is the situation in the inactivation of cytochrome P-450 in microsomal membranes.[50] The heterogeneity of cytochrome P-450 in liver microsomes leads to a break on the kinetic curves in the semilogarithmic form, reflecting the inactivation of different forms or different conformers of cytochrome P-450 (Fig.2). In this case the time variation of the concentration of the catalytically active cytochrome is represented by the sum of two exponential functions. The rate constant k_{in}, determined graphically for the first process stage from the semilogarithmic form of the kinetic curve, approaches its true value provided that the rate of inactivation in the second stage is much lower than in the first.

Yet another cause of complication of the kinetics of the inactivation of monomeric proteins is their association (aggregation) in buffer solutions.[3,20,21,51] As a rule, inactivation with formation of aggregates is described by the two-stage kinetic scheme[51] $\mathrm{E} \rightleftarrows \mathrm{D} \rightarrow \mathrm{I}$, in which E is the native form, E the denatured form, and I the inactivated form (aggregate). Evidently, this scheme does not differ formally from scheme (2).

Examination of extensive experimental data on the inactivation of monomeric and oligomeric (subunit) proteins led Arens et al.[33] to the conclusion that the inactivation of all proteins can be described by a general formal scheme which is identical with scheme (2). The first reversible stage reflects the dissociation of subunit proteins and the conformational changes (denaturation) in monomeric proteins. The presence of the first reversible stage leads in both cases to the appearance of breaks in the kinetic curves for the inactivation of enzymes recorded in the low-temperature region, i.e. these curves are not described by a first-order equation over the entire time interval.[24-32] The positions of the breaks depend on the initial protein concentration in solution.[24-31]

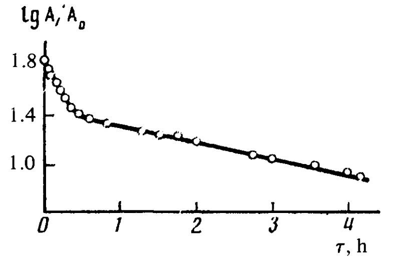

Figure 2. The semilogarithmic form of the kinetic curve for the inactivation of cytochrome P-450 in rabbit liver microsomes at 52 °C in tris-HCl buffer at pH 7.54.[50]

The complete kinetic characterisation of the protein inactivation process [scheme (2)] presupposes the determination of the rate constants for the forward (k_1 and k_2) and reverse (k_{-1}) reactions, the equilibrium constant between the native enzyme E and its denatured form A ($K = k_1/k_{-1}$), and also the expressions, in an integral form, for the concentrations of E and A at a specific instant. Analysis of scheme (2) subject to the initial conditions $t = 0$, $[E]_0 = a$, and $[A]_0 = [I]_0 = 0$ yields the following expressions for the current concentrations of E and A:[52]

$$E = a\left\{\frac{\lambda_2 - k_1^{-1}k_2}{\lambda_2(\lambda_2-\lambda_3)}e^{-\lambda_2 k_1 t} + \frac{k_1^{-1}k_2-\lambda_3}{\lambda_3(\lambda_2-\lambda_3)}e^{-\lambda_3 k_1 t}\right\}$$

$$[A] = a/\lambda_2 - \lambda_3\cdot(e^{-k_1\lambda_3 t} - e^{k_1\lambda_2 t}), \text{ where } \lambda_2 = {}^1/_2(\alpha+\beta);$$

$$\lambda_3 = {}^1/_2(\alpha-\beta);\ \alpha = 1 + k_{-1}/k_1 + k_2/k_1;\ \beta = [\alpha^2 - 4k_2/k_1]^{1/2}$$

Evidently the current concentrations of the E and A forms of the protein are described by extremely complex equations. We may note that in practice it is frequently impossible to measure the concentrations of the protein forms A and I and one usually follows only the consumption of the initial enzyme E.

The system of equations describing scheme (2) and other similar schemes is non-linear and has no analytical solution.[30,32] In a series of studies[24-32] dealing in detail with the kinetics of the inactivation of oligomeric enzymes, Poltorak, Chukhrai, and co-workers therefore proposed several procedures for the approximate solution of the equations for the determination of the kinetic constants k_1, k_{-1}, and k_2 and the dissociation constants of the subunit enzymes K. One of the versions of the approximate solution makes it possible to obtain the rate constant for the dissociation of the oligomeric protein from the equation[31,32]

$$2(v/v_0) - {}^1/_2(v/v_0)^2 = {}^3/_2 - k_1 t \ , \qquad (4)$$

where v_0 and v are the rates of inactivation of the protein in the initial instant and after time t, which must not exceed the time τ corresponding to the break in the plot of ln v against t. In the second version of the approximate description of the kinetics of the inactivation of subunit enzymes, the following equation is used:[30-32]

$$(1/t)\ln v/v_0 = -k_1 + ({}^4/_3)k_1^2k_{-1}[E]_0 t^2 \ , \qquad (5)$$

in which $[E]_0$ is the initial concentration of the enzyme and the time t must also be less than τ. The linearisation of the kinetic inactivation curves with the aid of Eqn.(5) makes it possible to calculate not only the rate constant k_1 but also the rate constant k_{-1} for the reverse reaction and then also the constant for the dissociation of the subunit proteins into monomers or dimers in the thermal transformation of the tetrameric protein. Eqns.(4) and (5) have been used successfully to characterise kinetically the inactivation processes involving kidney acylase,[29] alkaline phosphatase,[31] and certain other oligomeric proteins.

Thus a correct kinetic description of the inactivation of enzymes with an arbitrary choice of the initial concentration reduces to a complex analysis of the kinetic curves, since their semilogarithmic forms have breaks, while the effective rate constants k_{in}, calculated with the aid of such semilogarithmic forms, are as a rule functions of the initial protein concentration and therefore strictly speaking are not constants. It is therefore necessary to seek methods for the approximate solution of the system of equations describing the associative-dissociative scheme (2) in order to find simple ways of linearing the kinetic relations.

Does this imply that there can be no cases where the kinetic curves for the thermal inactivation of enzymes can be linearised in terms of plots of ln v against t? In our view this is not so, since protein inactivation conditions such that the reversible dissociation of the subunit enzyme or the first reversible stage of the conformational transformation of the monomeric protein are reduced to a minimum or are altogether absent have been realised in practice.

First case. The subunit enzyme has been treated with bifunctional reagents and its reversible dissociation into monomers is difficult.[14,15,29,34] For example, kidney acylase modified by glutaraldehyde is inactivated in accordance with a first order law, since the stage involving the reversible dissociation of the enzyme has been virtually ruled out.[29] In this case, the semilogarithmic forms of the kinetic curves show no breaks of any kind when inactivation is continued up to extremely advanced stages.

Second case. The subunit enzyme dissociates into monomers via an "all or nothing" mechanism and the process is accompanied by the complete loss of catalytic function. As an example, one may quote the dissociation of tetrameric catalase into monomers in acid and alkaline media,[35] on treatment with denaturing agents,[53,54] in the course of lyophilisation,[55] and as a result of the introduction of succinyl groups into the protein by treatment with succinic anhydride.[36] Regardless of how the dissociation of catalase is initiated, this process is accompanied by the loss of catalase activity and its kinetics obey a first-order law even for high degrees of inactivation.[35,36,56]

Third case. The dissociation of the subunit protein into monomers is the rate-limiting stage of the entire inactivation process. In the study of an NAD-dependent hydrogenase, the validity of the dissociative scheme for the thermal inactivation of this tetrameric protein was demonstrated:[38]

$$E_{4\text{-in}} \xleftarrow{k_i} E_4 \overset{k_1}{\rightleftarrows} 2E_2 \xrightarrow{k_d} E_{2\text{-in}},$$

where k_i and k_d are the inactivation and denaturation rate constants. The authors showed[38] that the rate of inactivation of the enzyme is determined by the dissociation of the tetramers into dimers. The semilogarithmic forms of the kinetic curves describing the loss of activity by hydrogenase therefore have no breaks up to considerable degrees of inactivation of the protein. In the case of monomeric proteins, there is also a possibility of inactivation pathways in which the rate of the entire process is limited by the first stage. Such examples will be presented below.

Fourth case. The protein is inactivated in highly dilute solutions where the association of the enzyme subunits or the aggregation of the monomeric protein is hindered or reduced to a minimum. In this case, subject to the condition that the rate-limiting stage of the entire process is the first reaction stage [see Scheme (2)], the inactivation kinetics obey a first order law and the semilogarithmic form of the kinetic curves should have no breaks of any kind.

We shall consider next the kinetics of the inactivation of proteins whose transformations under different conditions have been investigated in our laboratory.[35,36,47,50,56–70] They include monomeric (lysozyme,[47] myoglobin,[60] cytochrome b_5,[63,69] horseradish peroxidase,[61,62] and cytochrome P-450 LM-2[50,64,66–69]) and subunit biopolymers (lactate dehydrogenase,[58] malate dehydrogenase,[59] and catalase[35,36,56]). The thermal inactivation of all the proteins enumerated was studied

Table 1. Thermodynamic activation parameters for the irreversible inactivation of enzymes in different media.

Enzyme	Inactivation conditions	Δt[a]	E_{act}, kcal mol^{-1}	t° C	ΔH^*, kcal mol^{-1}	ΔS^*, cal mol^{-1} K^{-1}	ΔG^*, kcal mol^{-1}	Refs.
Glucose-6-phosphate dehydrogenase,	0.1 M NaOH-glycine buffer, pH 9.1	23—46	4.34; 131.40	25 45	3.75; 130.80	—70.20; 341.00	24.66; 22.40	[57]
EC 1.1.1.49	Inverted micelles; 0.1 M AOT[c] 0.1 M Triton X-45, 12% of 0.1 M NaOH-glycine buffer, pH 9.1	23—46	19.40; 61,42	25 45	18.80; 60.80	—18.15; 118.80	24,20; 23.02	[57]
Lysozyme, EC 3.2.1.17	0.067 M phosphate buffer, pH 6.2	20—80	24.20	37	23.60	—7.50	25.90	[47]
Lactate dehydrogenase, EC 1.1.1.27	0.1 M phosphate buffer, pH 8.2	20—60	6.40: 44.60	25 37	5.81 44.00	—60.06 63,50	23.70 24.40	[58]
Malate dehydrogenase, EC 1.1.1.37	0.1 M phosphate buffer, pH 8.2	20—52	43.00	37	42.40	63,60	22.70	[58,59]
Myoglobin from sperm whale heart	0.05 M phosphate buffer, pH 7.4	46—71	17.70	25	17,10	—	—	[60]
	The same buffer with sodium cholate	22—37	17.10	25	16.50	—22.60	23.20	[60]
	The same buffer with Twin 20 and 15% of glycerol	30—46	31.80	25	31.20	—24.00	24.00	[60]
Catalase, AC 1.11.1.6	0.1 M phosphate buffer, pH 6.6	20—45	14.60	40	14.00	—30.20	23,43	[56]
Complex of catalase with strophanthin K	The same buffer	20—45	22,80	40	22.20	—4.20	23.50	[56]
Catalase subunits	0.1 M phosphate buffer, pH 3.28	22—40	14.70	37	14.10	—23.50	21.40	[35]
Succinylated catalase	0.1 M citrate-acetate buffer, pH 6.0	31—65	15.50	—	—	—	—	[36]
Horseradish peroxidase, EC 1.11.1.7	0.1 M citrate-acetate buffer, pH 6.0	37—53	19.90	45	19.20	—14.90	24.00	[61]
Complex of peroxidase with strophanthin K	The same buffer	37—53	20,60	45	19.90	—12.80	24.00	[61]
Horseradish peroxidase	0.05 M phosphate-citrate buffer, pH 7.0	45—80	47.40	45	46.77	64.71	26.19	[62]
	Inverted micelles: 0.2 M AOT, 6% of 3 mM phosphate-citrate buffer, pH 4.6	26—50; 50—60	26.40; 62.20	45; 50.5	25.77; 61.56	6.33; 122.60	23.76; 21.90	[57.62]
	Inverted micelles: 0.1 M AOT, 0.1 M Triton X-45, 6% of the same buffer, pH 4.0	19—55; 55—66	5,30; 62.40	45	4,67	—61.42	24.20	[57.62]
Cytochrome b_5 from rabbit liver	0.05 M tris-H_3PO_4 buffer, pH 7.5 with 15% of glycerol	50—62	4.80	50.5	4.16	—63.84	24.80	[63]
	Inverted micelles: 0.25 M AOT, 4.5% of the same buffer	32—39	2.00	37	1.39	—71.75	23.63	[63]
	Inverted micelles: 0.13 M AOT, 0.13 M Triton X-45, 4.5% of the same buffer	31—37	6.60	37	6.00	—54.74	23.00	[63]
Cytochrome P-450 LM-2, EC 1.14.14.1	0.05 M Tris-HCl buffer, pH 7.54, with 20% of glycerol	40—58	23.50	45	22.86	—7,25	25.17	[50]
Cytochrome P-450 immobilised on polyamide	The same buffer	40—58	22.40	45	21,76	—8.47	24.46	[50]
Cytochrome P-450 in microsomes	0.05 M phosphate buffer, pH 7.33, with 0-4.1 M glycerol	45—54	111.0—54.0	50.4	110.0—53.0	280 0—89 0	19.70—24.80	[64.65]
	0.05 M tris-HCl buffer, pH 6.88, with 0-4.1 M glycerol	45—54	110.0—98.0	50.5	109,0—97,0	265.0—220.0	23.80—26.20	[64,65]

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[a] Δt = temperature range.

[b] The temperatures for which the thermodynamic parameters were calculated.

[c] AOT = Aerosol OT (sodium salt of di-2-ethylhexyl ester of sulphosuccinic acid).

Pairs of activation parameters are quoted in those cases where the temperature variations of the constants exhibit a break in the Arrhenius plots.

in buffer solutions and, for some of them (peroxidases,[57,62] glucose-6-phosphate dehydrogenase,[57] cytochrome b_5,[68,69] and cytochrome P-450 LM-2[66-69]), in inverted surfactant micelles in organic solvents. The thermal inactivation of the integral membrane enzyme cytochrome P-450 LM-2 was studied in biomembranes (liver microsomes).[50,64,65] Among the test objects, there are water-soluble (lysozyme, peroxidase, catalase, myoglobin, and dehydrogenases) and hydrophobic biopolymers (cytochromes b_5 and P-450), as well as modified enzymes (succinylated catalyse,[36] systems obtained by coupling strophanthin K to peroxidase,[61] and catalase[56]). The choice of these test objects was dictated not only by fundamental research but also the wide-scale employment of the majority of them in practice.[71-73] The proteins which we investigated, the conditions and temperatures ranges in which they are inactivated, and the thermodynamic activation parameters are listed in Table 1.

We confined ourselves to a quantitative examination of data obtained solely in our laboratory, although Table 1 might have been supplemented by the results of studies of other groups in our country[14,15,19,20-34,74,75] and abroad.[17,76-80] This limitation of the range of kinetic studies of the thermal inactivation of proteins (enzymes) considered is due to the following causes: firstly, the data of other workers have already been surveyed and examined critically in earlier publications[14,15,19-22] or in the course of the preparation of the present review[74,75] and in our view does not require a fresh analysis; secondly, the quantitative characteristics of thermal inactivation have been frequently obtained by different workers under different conditions, so that it is sometimes difficult to establish the initial concentrations of the proteins subjected to thermal inactivation, which leads to contradictory results when the effective kinetic constants are referred to particular stages of the protein inactivation and reactivation processes investigated, which have been analysed, for example, in a recent monograph.[81] Analysis of the kinetic constants for the thermal inactivation of proteins without referring them to the initial concentrations of the inactivated objects is incorrect, as will be shown below, and can lead to erroneous conclusions about the character and mechanism of the thermal inactivation of biopolymers. We have therefore confined ourselves to a quantitative consideration of our own data, since the results analysed here have been obtained under controlled conditions, which can be readily compared for different objects in different media.

III. KINETICS OF THE INACTIVATION OF ENZYMES IN DIFFERENT MEDIA

1. Kinetics of the Inactivation of Enzymes in Aqueous Media

Lysozyme (EC 3.2.1.17) is inactivated in accordance with scheme (2).[41,44-47] At protein concentrations in the range 0.14–5.48 M (in the temperature range 40–70 °C), the first order rate constant depends on the initial concentration (Fig.3), the dependence being described by the equation

$$k_{in} = k_0 \exp(-\alpha[E]_0) \, , \tag{6}$$

where $[E]_0$ is the initial protein concentration, k_0 the inactivation rate constant at infinite dilution of the protein which is independent of $[E]_0$, and α a coefficient which depends on temperature and has the dimensions of the reciprocal of concentration.[47] The temperature variation of α (Fig.3) is described by the equation

$$\alpha = \alpha_0(1 - \gamma/T) \tag{7}$$

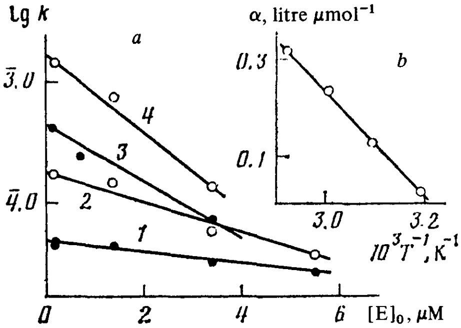

Figure 3. *a*) Dependence of the effective rate constants for the inactivation of lysozyme on its initial concentration at different temperatures (°C): *1*) 40; *2*) 50; *3*) 60; *4*) 70; *b*) temperature dependence of α.[47]

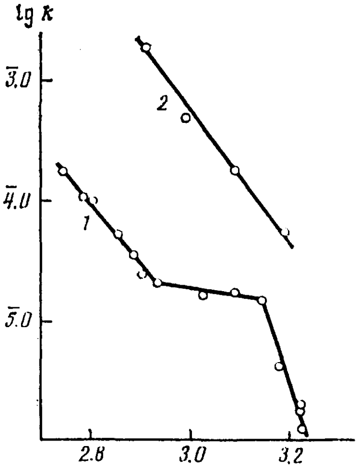

Figure 4. Temperature dependence of the rate constants for the inactivation of lysozyme at a concentration of 0.20 mg ml⁻¹ (curve *1*) and at infinite dilution of the enzyme (curve *2*).[47]

The temperature variation of the effective inactivation rate constants k_{in} at high lysozyme concentrations is characterised by breaks in the Arrhenius plot (Fig.4), while the temperature variation of the rate constants k_0, obtained by extrapolating k_{in} to zero protein concentration, does not exhibit breaks (Fig.4, line *2*). E_{act} and the expression for the rate constants in a general form can be found from Fig.4 (line *2*):[47]

$$k_0 = 4.0 \times 10^{11} \exp(-24\,200/RT) \, . \qquad (8$$

From Eqns.(6)–(8), we obtain a general expression for the effective rate constant k_{in}:[47]

$$k_{in} = 4.0 \times 10^{11}\exp\{-24\,200/RT-\alpha_0(1-\gamma/T[E]_0\} \quad (9)$$

Evidently, the temperature dependence of k_{in} is not described by the Arrhenius law, since k_{in} depends not only on temperature but also on the protein concentration $[E]_0$. The correct kinetic constant characterising the inactivation of lysozyme can only be k_0, since it does not depend on the protein concentration in solution.

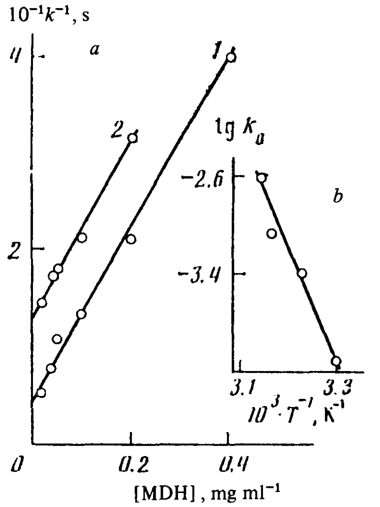

Figure 5. *a*) Dependence of the effective rate constants for the thermal inactivation of malate dehydrogenase (MDH) on the initial enzyme concentration at 45 °C (curve *1*) and 43 °C (curve *2*); *b*) temperature dependence of the rate constant k_0 for the inactivation of malate dehydrogenase corresponding to the infinite dilution of the protein.[59]

Malate dehydrogenase (EC 1.1.1.37) is inactivated in accordance with a scheme analogous to scheme (2):

$$E_2 \overset{k_1}{\rightleftarrows} 2E \xrightarrow{k_d} E_d,$$

in which E_2 is the dimer, E the enzyme subunit, k_1 the rate constant for the dissociation of the dimer, and k_d the rate constant for the denaturation of the subunit.[59] For an arbitrarily selected protein concentration, the inactivation rate constants k_{in}, evaluated from the semilogarithmic forms of the kinetic curves describing the decrease of the activity of the enzyme, depend on the initial dimer concentration (Fig.5):[59]

$$k_{in} = k_0/(1+\alpha k_0[E_2]_0) \quad (10)$$

where k_0 is the rate constant for the inactivation of the protein at infinite dilution and α is a constant which depends on temperature and has the dimensions of the reciprocal of the rate (litre mol^{-1} s). The temperature variation of the rate constant for the inactivation of malate dehydrogenase k_0 (Fig.5) is described by the equation:[59]

$$k_0 = 1.42 \times 10^{27}\exp(-43\,000/RT) \quad (11)$$

The temperature variation of the effective rate constants k_{in} is not described by the Arrhenius equation, since they depend on temperature, the enzyme concentration, and the coefficient α.

Table 2. The rate constants k_{in} for the inactivation of malate dehydrogenase (MDH), calculated from the lg ν–time relations,[59] and the rate constants k_1 calculated from Eqn.(4).[31,32]

$[MDH]_0 = 0.01$ mg ml^{-1}			$[MDH]_0 = 0.05$ mg ml^{-1}		
t° C	$10^4 k_{in}$, s^{-1}	$10^4 k_1$, s^{-1}	t° C	$10^5 k_{in}$, s^{-1}	$10^5 k_1$, s^{-1}
20	0.128	0.139	28	0,798	1.670
25	0.294	0.278	30	3.220	2.900
26.5	0.319	0.296	34	10.01	9.52
28	0.437	0,389	37	11.70	12.30
30	0,511	0.407	38	11.80	12.50
34	0.766	0.714	40	19.30	17.20
37	1,440	1.480	43.5	69.00	62.50
40	2.920	3.180	46	115,00	105.00
45	9 590	9.170	49	478.00	400.00

It is of interest to compare the effective rate constants k_{in}, calculated for different initial protein concentrations and temperatures, with the rate constants k_1 (see the inactivation scheme presented above) calculated from Eqn.(4).[31,32] Table 2 compares the values of k_{in} and k_1 under different conditions. At low enzyme concentrations, the two constants differ little, but, with increase of the concentration of malate dehydrogenase by a factor of 5, the difference between them becomes significant. We believe that the agreement between k_{in} and k_1 at low protein concentrations is not fortuitous. The stage involving the dissociation of the enzyme dimers is rate limiting in its inactivation and the reverse stage, involving the reassociation of the malate dehydrogenase subunits at low enzyme concentrations, is difficult or does not occur at all. Nor can one rule out the possibility that the inactivation is limited by the conformational changes in the dimer, occurring when it dissociates into subunits.

Lactate dehydrogenase (EC 1.1.1.27). It is a tetrameric enzyme, whose inactivation can be described by several schemes with successive dissociation into dimers and monomers.[58] In the temperature range 20–60 °C, the effective inactivation rate constant depends on the initial concentration of the tetramer E_4. This dependence is described by Eqn.(10), in which the concentration of the dimer E_2 has been replaced by the concentration of the tetramer E_4. In the range 35–60 °C, the temperature dependence of k_0 obeys the equation:[58]

$$k_0 = 1.30 \times 10^{27}\exp(-44\,600/RT) \quad (12)$$

Below 35 °C, E_{act} falls to 6.40 kcal mol^{-1}.

Catalase (EC 1.11.1.6) from ox liver. The dissociation of the enzyme obeys the "all or nothing" principle: $E_4 \overset{k_1}{\rightleftarrows} 4E$.[53,54] The enzyme subunits lack catalase activity.[35,36,53,55] The constant for the dissociation of catalase into subunits k_1 depends strongly on the pH and is described by Eqns.(13) and (14) respectively in acid and alkaline media:[35]

$$k_1 = 5.0 \times 10^7[H^+]^{2.3}, \quad (13)$$

$$k_1 = 5.0\,[H^+]^{-1.4} \quad (14)$$

In 0.1 M phosphate buffer at pH 6.6 at temperatures in the range 20–45 °C, the thermal inactivation of catalase (investigated in terms of the loss of its catalytic activity in the oxidation of ethanol by cumenyl hydroperoxide) is characterised by $E_{act} = 14.6$ kcal mol^{-1}. After its modification by 11 molecules of strophanthin K, the activation energy for the thermal degradation of the enzyme increases to 22.8 kcal mol^{-1}.[56] The temperature variation of the rate constant for the inactivation of catalase in the range 20–45 °C is described by the equation[56]

$$k_1 = 4.13 \times 10^6 \exp(-14\,600/RT)\ .$$

Horseradish peroxidase (EC 1.11.1.7). The temperature variation of k_{in} for the enzyme is described by the equation[61]

$$k_{in} = 1.7 \times 10^{10} \exp(-19\,900/RT)\ .$$

The modification of peroxidase by three strophanthin K molecules alters little the activation characteristics for the inactivation of the enzyme (Table 1). A change in the pH has a marked influence on the rate constant for the inactivation of peroxidase and the activation characteristics of the process: in 0.1 M citrate-acetate buffer at pH 6.0, the activation energy is 19.9 kcal mol^{-1},[61] while in 0.05 M phosphate-citrate buffer pH 7.0 it increases to 47.4 kcal mol^{-1}.[62]

Cytochrome P-450 LM-2 (EC 1.14.14.1). In tris-HCl buffer (pH 7.54) with 20% of glycerol, the enzyme loses its catalytic activity in the range 40–58 °C. $E_{act} = 23.5$ kcal mol^{-1} corresponds to this process.[50] It is important to note that the loss of catalytic activity is accompanied by the simultaneous decrease of the intensity of the Soret band of the carbonyl complex of cytochrome P-450 and by the appearance of a spectral band at 420 nm, corresponding to the inactive form of the haemoprotein, namely P-420.[65,82] The immobilisation of cytochrome P-450 LM-2 on polyamide does not induce an appreciable change in E_{act} for the thermal degradation of the haemoprotein (22.4 kcal mol^{-1}).[50] The kinetic curves for the decrease of the catalytic activity of cytochrome P-450 LM-2 in solution as a rule correspond to several stages which can be accounted for in two ways: firstly, the highly hydrophobic cytochrome P-450 forms aggregates in aqueous solution in which it is inactivated at different rates; secondly, in dilute solutions the inactivation of different conformers of the same form of cytochrome P-450 may be manifested, since after extraction from microsomal membranes the haemoprotein is unusually labile in aqueous media.

2. Kinetics of the Inactivation of Enzymes in Inverted Surfactant Micelles in Organic Solvents

Inverted surfactant micelles, in which enzymes and proteins are incorporated, constitute a realistic model of biological membranes, reflecting many important aspects of their structure and complex lipid–protein and protein–protein interactions.[66–69,83–85] Furthermore, microheterogeneous (protein-surfactant–water–organic solvent) systems constitute an extremely interesting medium for enzymic reactions.[83–85] It has been frequently demonstrated that enzymes of different classes, solubilised by inverted surfactant micelles, not only retain their catalytic properties but are sometimes more active than in aqueous media.[69,83–86] For the practical use of proteins in inverted surfactant micelles, it is important to know not only the catalytic activity of the biocatalysts under these conditions but also their stability at different temperatures and pH and on exposure to the influence of denaturing additives. We have shown that the stability of haemoproteins in inverted surfactant micelles depends on temperature, pH, ionic strength, and protein stabilising additives, as in aqueous media; the stability of haemoproteins is also influenced by the physicochemical properties and composition of the micelles, by the specific alteration of which it is possible to stabilise significantly the solubilised proteins.[66–69,83–85]

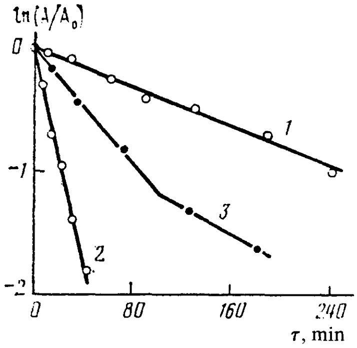

Figure 6. Semilogarithmic forms of the kinetic curves for the inactivation of glucose-6-phosphate dehydrogenase at 40 °C: *1*) buffer solution; *2*) AOT micelles in heptane; *3*) mixed AOT–Triton X-45 micelles in heptane;[57] the conditions are indicated in Table 1.

Glucose-6-phosphate dehydrogenase (EC 1.1.1.49, G6PDH) is inactivated in inverted AOT micelles (AOT = sodium salt of di-2-ethylhexyl ester of sulphosuccinic acid) in heptane in accordance with a first-order kinetic law up to high degrees of inactivation (Fig.6).[57] We may note that the enzyme is inactivated in aqueous solutions also in accordance with the same law. However, in mixed micelles made up of AOT and Triton X-45 (1:1), the inactivation of the enzyme deviates from the first-order law (Fig.6). The temperature variation of the effective rate constants for the inactivation of G6PDH in the range 23–46 °C is characterised by a break in the Arrhenius plot at 34 °C. The activation energy is $E_{act} =$ 61.4 kcal mol^{-1} above the break and 19.4 kcal mol^{-1} below it.[57] On inactivation of the enzyme in aqueous solutions, a break is also observed at 36 °C and E_{act} differs from the values calculated for micellar systems (Table 1).

Horseradish peroxidase exhibits a "periodicity" in the variation of its activity on inactivation in inverted AOT micelles and in mixed micelles comprising AOT and Triton X-45, which we attribute to complex cooperative transformations of the "water–protein–AOT–heptane" system.[57,62] This "periodicity" in the inactivation of the peroxidase is smoothed out on raising the temperature to 50–55 °C (Fig.7). We may note that in buffer solutions the inactivation of peroxidase is described by a first-order kinetic equation (Fig.7b, lines *5* and *6*),[57,61,62] i.e. the phenomenon of "periodicity" in the variation of the catalytic activity of the enzyme is associated solely with the nature of the inverted surfactant micelles. The rate constants for the inactivation of the peroxidase in micelles are also influenced by the concentration of the buffer, its pH, the percentage content of the aqueous phase, and the addition of the non-ionic detergent Triton

X-45 or glycerol to the system.[57,62] The temperature variation of the effective rate constants for the inactivation of the peroxidase in micelles is characterised by a break at 55 °C in the Arrhenius plot, and the values of E_{act} above and below this temperature differ markedly (Table 1).

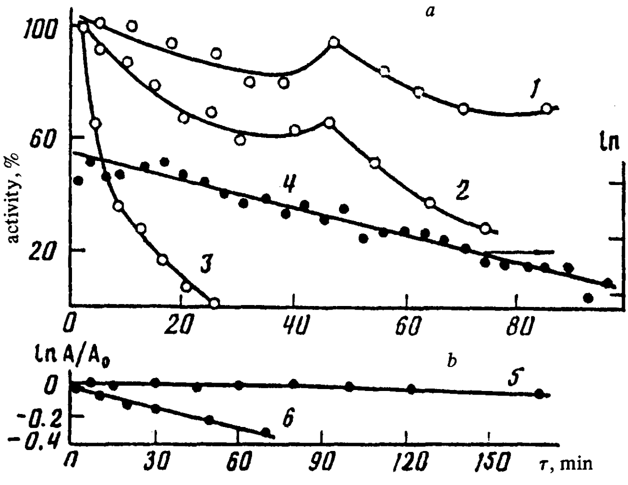

Figure 7. Kinetic curves for the variation of the catalytic activity of peroxidase in inverted micelles; 0.2 M AOT, 6% of polar phase comprising 0.05 M phosphate-citrate buffer at pH 4.6 (13.5 nM enzyme): *a*) temperature (°C) [*1*) 37; *2*) 43; *3*) 54; *4*) semilogarithmic form of the kinetic curve at 40 °C]; *b*) semilogarithmic forms of the kinetic curves for the variation of the activity of peroxidase (13.5 nM) in 0.05 M phosphate-citrate buffer at pH 7.0 at different temperatures (°C) [*5*) 45; *6*) 55].[57]

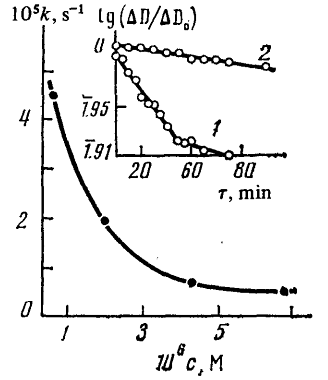

Figure 8. The influence of the concentration of cytochrome b_5 (*c*) on the rate constant for its transformation in AOT micelles in octane at 31 °C; cytochrome b_5 concentration (μM): *1*) 0.68; *2*) 6.84; (0.25 M AOT, 45% of polar phase in octane).[63]

Cytochrome b_5 is inactivated in inverted micelles at rates which depend on its initial concentration (Fig.8). At low protein concentrations, the breaks in the semilogarithmic forms of the kinetic curves describing the decrease of the intensity of the Soret band are absent but they appear on raising the concentration of the haemoprotein.[63] The character of the variation of k_{in} with the initial concentration is the same for both cytochrome b_5 in micellar systems and for malate and lactate dehydrogenases in aqueous solutions [Eqn.(10)]:[59] with increase of the concentration of the protein, the rate constant for its inactivation diminishes.

Cytochrome P-450 LM-2 is inactivated at different rates in micelles of different composition.[66-69] By increasing the complexity of the micelles, it is possible to achieve a significant stabilisation of this labile protein in micellar systems. At 40 °C, k_{in} for cytochrome P-450 in micelles containing AOT, cetyltrimethylammonium bromide, Twin 20, and Triton X-45 is 2.9×10^{-6} s^{-1}, while in liver microsomes at the same temperature it is 3.4×10^{-6} s^{-1},[66,67] i.e. the stability of the haemoprotein in a specifically selected micellar system can be actually greater than its stability in the native membrane.[66,67,69]

Thus the inverted surfactant micelles not only protect proteins against the denaturing influence of organic solvents but in certain cases are capable of ensuring their relatively high thermal stability in a hydrocarbon medium.[66-69] The optimum composition of the inverted micelles ensuring the retention of the catalytic activity of the enzyme or even its increase is specific to each protein. However, the thermal stability of enzymes in micelles is usually lower than in an aqueous medium, although enzymes in micellar systems can be stabilised by increasing the complexity of the composition of the micelles in such a way that the stability of the enzyme reaches a level characteristic of buffer solutions. For example, at 45 °C the rate constant for the inactivation of G6PDH in a buffer solution is 2.24×10^{-3} s^{-1}, while in mixed 1:1 micelles comprising AOT and Triton X-45 it is 9.12×10^{-4} s^{-1}, i.e. the enzyme is 2.4 times more stable in the micelles.[57] Yet another way of stabilising proteins in organic solvents has been proposed recently:[87] by the covalent incorporation of α-chymotrypsin in particles of cross-linked polyacrylamide gel with colloidal dimensions (100–400 Å). This catalyst is universal and can be used in both hydrocarbon and aqueous solutions.

The quantitative description of the inactivation of proteins and micelles is associated with the same difficulties as in aqueous solutions: the effective inactivation rate constants depend on the initial protein concentration;[63,70] the tempera-true variation of these constants is complicated by breaks in the Arrhenius plots, which reflect not only the effective character of the rate constants but also the characteristic features of the behaviour of the micellar systems as the temperature is raised.[57,62,70]

3. Kinetics of the Inactivation of Cytochrome P-450 in Microsomal Membranes

Cytochrome P-450 is the terminal oxidase in many hydroxylating multienzyme systems, widely distributed in nature.[82] These systems are responsible for the hydroxylation of hydrophobic compounds to form more polar hydroxy-derivatives, which are either removed from the organism or serve as key compounds in the biosynthesis of bioactive substances.[82] The majority of cytochromes P-450 are associated to different extents with membranes and are distinguished by a high lability after extraction from the native environment. The unique ability of cytochrome P-450 to catalyse the conversion of a wide variety of compounds into hydroxy-derivatives has led investigators to seek ways of the practical utilisation of this family of biocatalysts. However, the difficulty of isolating the cytochromes from the membrane, their low stability in aqueous media, the high cost of the source of the raw material, and also the multienzyme nature of the hydroxylating systems have made it necessary to seek procedures whereby stabilised organelles (microsomes, mitochondria) could be used in enzymic hydroxylation processes *in vitro*.[88,89] It is therefore a matter of great urgency to be able to characterise the inactivation of cytochromes P-450 in native membranes and to stabilise them in this medium.[50,64,65,82,88,89] We investigated the inactivation of cytochrome P-450 in rabbit liver microsomes on the basis of the loss of its catalytic activity in the oxidation of aniline and the variation of its spectroscopic properties.[50,64,65]

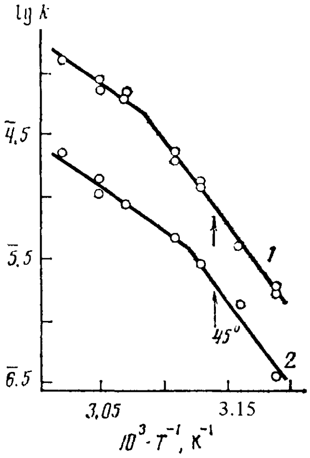

Figure 9. Temperature dependence of the rate constants for the thermal inactivation of cytochrome P-450 in rabbit liver microsomes in the absence of glycerol from the solution: *1*) first stage of the process; *2*) second stage of the process.[50]

The decrease of the catalytic activity of the haemoprotein in microsomes is accompanied by a decrease of the intensity of the Soret band of its CO complex and an increase of the concentration of the inactive form of the haemoprotein—cytochrome P-420.[65] The change in the activity of cytochrome P-450 in microsomes takes place in several stages.[64] As a rule, the effective rate constant has been determined solely for the first stage of the process. The temperature variation of k_{in} for cytochrome P-450 in microsomes is characterised by a break in the Arrhenius plots for the first and second stages of the haemoprotein inactivation process (Fig.9).[50] The causes of the appearance of the breaks will be discussed below. One of the ways of stabilising membrane proteins, and cytochrome P-450 in particular, is by incorporation in lipid dispersions and liposomes, modelling many aspects of native biological membranes. This problem is discussed in detail in a monograph.[90] The study of the thermodynamic characteristics of the thermal inactivation of cytochrome P-450 in liposomes showed that they depend on the pH and temperature and vary, compared with aqueous solutions, in the following ranges: ΔH from 78 to 80 kcal mol^{-1} and ΔS from −163 to −184 cal mol^{-1} K^{-1}. This indicates an increase of the conformational "rigidity" of the protein in liposomes compared with buffer solutions.[91]

An important task in the study of the thermal inactivation of enzymes is the correlation of the kinetic characteristics of the rate-limiting stage of this complex process and its molecular mechanism. The solution of this problem by kinetic procedures alone is impossible and requires the use of many other methods (electronic, circular dichroism, and NMR spectroscopy, sedimentation analysis, and electrophoresis). The application of a set of physicochemical methods makes it possible in many instances to relate the rate-limiting stage of the thermal inactivation to fairly definite molecular mechanisms of the transformations of the biopolymer. It has been already noted that ^{13}NMR,[43] fluorescence,[45] and circular dichroism[46] data, measurement of the optical density of lysozyme,[42] and the study of the kinetics of its inactivation[44,47] suggest that the rate-limiting stage in the thermal inactivation of this protein is associated with the ionisation of the Glu-35 residue and the decomposition of the polypeptide chain along the 5–15 section.[47–49] The rate-limiting stage in the thermal inactivation of the more complex membrane enzyme cytochrome P-450 is the cleavage of the coordinate bond between the haem iron and the cysteine residue in the polypeptide chain, which transforms the enzyme into the inactive form P-420.[50,82,90] The determination of this rate-limiting stage became possible solely from a series of studies of the kinetics of the thermal inactivation of cytochrome P-450[50,65] and of the changes in its spectroscopic characteristics.[65,82,90]

Studies of Poltorak, Chukhrai and co-workers,[24–33,74] Berezin, Martinek, and Ugarova and co-workers[14,15,19–22,75] in our country and of Pfeil[17] and Jaenicke[76–80] abroad have been devoted to the solution of the complex problem of correlating the kinetic parameters and the structural changes in enzymes during their inactivation. Examination of these problems is very important but is outside the framework of this review, which is devoted solely to the kinetic aspects of the thermal inactivation of proteins and enzymes. We can only refer the reader to a recent review,[74] which deals in detail with the processes involving the dissociative thermal inactivation of enzymes and the approximate methods of calculation of the individual kinetic parameters of these processes and indicates ways whereby subunit enzymes can be stabilised by the fixation of their quaternary structure, and also to a review[75] devoted to the principal structural and physicochemical factors governing the stabilisation of protein macromolecules in solution and methods for the stabilisation of biocatalysts by chemical modification and point mutations of proteins. A useful critical analysis of studies concerning the correlation of the kinetic data for the inactivation and reactivation of subunit enzymes and their structural changes has been carried out in a monograph.[81]

IV. THE INFLUENCE OF POLYOLS AND DETERGENTS ON THE STABILITY OF ENZYMES IN SOLUTIONS

The medium in which proteins function in the living cell differs to a large extent in composition, viscosity, polarity, and other parameters from the solutions used *in vitro*. It has long been known that various organic solvents greatly reduce the stability of proteins. The addition of many low-molecular-weight compounds (salts, sugars, polyols, detergents, etc.) to protein solutions influences the stability of the proteins (enzymes), since such substances alter the properties of the solutions and the affinity of the protein for the solvent. The influence of certain low-molecular-weight additives on the thermal stability of proteins is analysed in this Section and the mechanism of the stabilisation of the proteins is discussed.

The stabilising effect of polyols on proteins is well known.[92–102] The degree of denaturation of ovalbumin by urea decreases in the presence of sucrose,[92] polyhydric alcohols increase the temperature of the thermal transition of lysozyme and ribonuclease,[93] and sucrose has a stabilising effect on egg proteins.[93] Various methods have been used to investigate the quantitative characteristics of the stabilising action of polyols on proteins:[98,100,101] systematic studies have been made of the influence of a series of polyols on the denaturation temperatures of ovalbumin, lysozyme, conalbumin, and α-chymotrypsinogen by the calorimetric method[98] and the interaction of a number of proteins with aqueous solutions of lactose and glucose has been studied in detail by the densitometric method.[100] In our laboratory a kinetic approach has been used to characterise quantitatively the influence of polyols on the thermal stability of various proteins.[58,61,64,65] The stabilising influence of polyols has been studied in relation to horseradish peroxidase modified with three strophanthin K molecules,[61] lactate dehydrogenase in aqueous solutions,[58] and cytochrome P-450 in rabbit liver microsomes.[64,65] Regardless of the nature of the protein (dissolved in water or hydrophobic) and its structural organisation (monomeric or subunit) and also regardless of the environment of the enzyme (aqueous solution or microsomal membranes), all the low-molecular-weight polyols and dextrans decrease the rate of inactivation of proteins.[58,61,64,65]

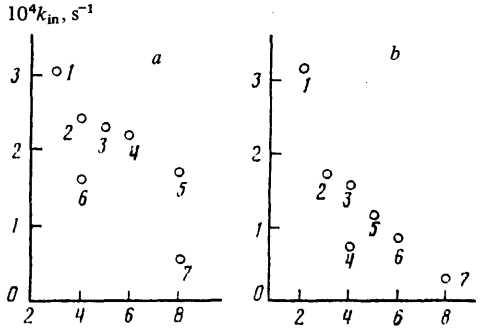

Figure 10. Variation of the rate constants for the thermal inactivation of horseradish peroxidase modified with strophanthin K (*a*) and of cytochrome P-450 in microsomes (*b*) with the number of OH groups in the polyol molecule; *a*: *1*) glycerol; *2*) rhamnose; *3*) glucose; *4*) sorbitol; *5*) maltose; *6*) xylose; *7*) sucrose; 50 °C;[61] *b*: *1*) ethylene glycol; *2*) glycerol; *3*) rhamnose; *4*) xylose; *5*) glucose; *6*) sorbitol; *7*) maltose; 50.5 °C.[64]

An increase of the concentration of glycerol and sugars in solution is accompanied by a monotonic decrease of the rate of inactivation of the peroxidase–strophanthin complex,[61] lactate dehydrogenase,[58] and cytochrome P-450 in microsomes.[64,65] Poly(ethylene glycols) 600, 1000, and 6000 and dextrans 20, 40, and 500 also stabilise the peroxidase–strophanthin complex.[61] However, dextran 20 and poly(ethylene glycols) 300 and 1000 have no stabilising effect on cytochrome P-450 in microsomes.[64] The question arises how the data concerning the stabilising action of polyols can be explained.

We showed that there is a direct relationship between the rate constants for the inactivation of the peroxidase complex and cytochrome P-450 and the number of OH groups in the molecules of stabilising additives (Fig.10): the greater the number of OH groups present in the stabiliser, the lower the value of k_{in}, i.e. the more stable the protein in solution or in microsomes.[61,64,65] In order to account for these data, we may recall the principal factors governing the stabilisation of proteins.[14,15,98] The stability of proteins is promoted by hydrogen bonds, electrostatic and hydrophobic interactions, and complex formation with certain metals. It is known that the dissolution of polyols in water has little effect on the formation of hydrogen bonds by proteins.[98] Electrostatic interactions are usually stronger in solutions of sugar than in water, but their contribution to the stabilisation of proteins is relatively small. The main factor stabilising the steric structure of proteins is hydrophobic interactions.[1–3,14,15,98] Such interactions are determined to a large extent by the nature of the solvent and hence depend greatly on the way that sugars and other polyols influence the structure of water. It has been shown that the interaction between pairs of hydrophobic groups is much stronger in solutions of glycerol and sugars than in pure water.[98] This is probably the main mechanism by means of which polyols stabilise proteins in aqueous solutions. The stabilising action of polyols is determined by the extent of their stabilising effect on aqueous solutions. The relative quantity $f = (\bar{V}_2 - V_w)/V_w$, where V_w is the van der Waals volume of the solute and $\bar{V}_2$ the partial molar volume of the same substance, including the internal volume of the molecule and the changes in the latter induced by the action of the solvent, has been suggested[98] as a structure formation characteristic of this kind. As an example we may quote of f for glycerol in water at 25 °C:[103] V_w = 51.4 ml mol^{-1}, $\bar{V}_2$ = 73.5 ml mol^{-1}, and f = 43.1%. The van der Waals volumes of sugars and other polyols have been calculated.[104] The following equation is used to determine the partial molar volumes $\bar{V}_2$:

$$\varphi_v = M_r/d_0 = 1000(d - d_0)/cd_0\ ,$$

where d and d_0 are the densities of the solution and the solvent, M_r is the molecular weight of the solute, and c the molar concentration of the solute in the solution.[98] Evidently ϕ_v varies linearly with c and extrapolation to zero concentration can yield the partial molar volume $\bar{V}_2$. The partial molar volumes of many sugars have been calculated in this way and have been published.[105] Sugars induce effective structure formation in water when their OH groups are oriented in space in such a way that the distance between them corresponds to the distance between the oxygen atoms in the molecular lattice of water.[98] More accurate quantitative characteristics of structure formation in water by polyols are not at present available.

There exist also other explanations of the stabilising effect of polyols on proteins. It has been suggested that polyol molecules can penetrate into the protein globules, which tends to intensify the hydrophobic interactions within the globule and to lower its lability.[99] In certain cases there is a possibility of specific binding of sugars and alcohols by proteins. For example, in the crystalline state lysozyme interacts with glucose, which stabilises the enzyme, since it is bound to it at at least two centres.[106] The constant for the binding of glucose to lysozyme is 2.3 M^{-1}.[106]

The stabilising influence of polyols on proteins of a wide variety of kinds indicates the principal role of the structure of the aqueous medium in which proteins are present and the secondary role of the structural organisation of the proteins themselves. It is of interest to analyse the influence of polyols on cytochrome P-450 in the microsomal membrane, i.e. in a microenvironment different to that in its aqueous solution.

Low-molecular-weight and high-molecular-weight polyols act on microsomes in different ways. The low-molecular-weight additives influence the membrane as mild surfactants: with increase of temperature, they penetrate into the lipid double layer, increase the degree of the hydration of phospholipids, lower the surface viscosity of the double layer, and increase the lateral mobility of the phospholipids.[107-110] High-molecular-weight additives poly(ethylene glycols) and dextran do not penetrate the lipid double layer, but they do reduce the surface potential of phospholipids and lead to the aggregation of vesicles;[111] by competing with phospholipids for water, they cause the contraction of the liquid crystal lattice of the double layer.[112] Thus low-molecular-weight polyols can act on the membrane as a whole, while high-molecular-weight polyols influence significantly only its surface layer. This can explain the different effect of polyols on the microsomal cytochrome P-450.[64,65] The stabilising effect of polyols must therefore be characterised taking into account their influence on the hydrophobic interactions in the protein globule and throughout the membrane as a whole. By penetrating into microsomes, glycerol promotes hydrophobic contact between pairs of non-polar groups of the cytochrome P-450 molecule, while in the regions near the membrane the polarity of the medium is reduced. Glycerol equalises the properties of the entire system and greatly increases the degree of structure formation in the medium. The considerable decrease of the entropy of activation with increasing glycerol concentration in the inactivation of microsomal cytochrome P-450 can be understood from this standpoint. On the other hand, glycerol decreases the enthalpy of activation for the thermal denaturation of cytochrome P-450 by acting on microsomes as a detergent and significantly facilitates the mobility and lability of the haemoprotein in the lipid double layer.[64,65] The influence of glycerol on the enthalpy of activation can be regarded as a destabilising factor in the thermal inactivation of cytochrome P-450, while the influence of glycerol on the entropy of activation is a stabilising factor in the thermal inactivation of the haemoprotein. It follows from our data that the ratio of these two factors favours the entropic factor, as a result of which the free energy of activation for the degradation of cytochrome P-450 in the presence of glycerol increases and the rate constant for the thermal degradation of cytochrome P-450 therefore diminishes. We may note that similar ratios of ΔH^* and ΔS^* have also been observed for other methods of stabilishing proteins, for example, when they are immobilised on carriers:[23] the binding to the matrix results in a deviation from the initial structure of the enzyme towards its denaturation, in a decrease of ΔH^*, and in a simultaneous decrease of ΔS^* as a consequence of the ordering of the structure of the immobilised protein.

Compared with polyols, detergents have a greater influence on proteins in aqueous solution. Systematic studies of the interaction of detergents with proteins in aqueous solutions are essential in view of their practical importance. Firstly, the use of detergents is inevitable in the isolation from membranes of the proteins bounds to them.[82,113-115] Secondly, the solubilisation of water-insoluble substrates of lipolytic enzyme is frequently necessary.[116] Thirdly, in order to attain high rates of enzymic reactions, non-ionic detergents are frequently added to buffer solutions.[117,118] In most cases the detergents are selected empirically. Extensive experimental data on the interaction of detergents with soluble and membrane proteins have been surveyed in a number of reviews.[115,119,120] However, the absence of systematic studies of the interaction of various detergents with proteins is still felt as an acute problem, which hinders the survey and assessment of the prospects for the development of this methodologically important field of enzymology.

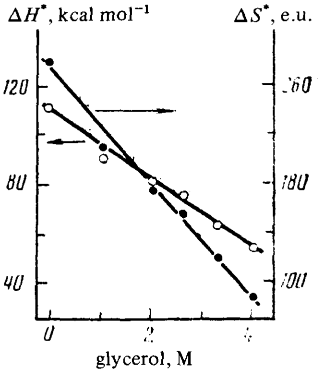

Figure 11. Dependence of ΔH^* and ΔS^* on the glycerol concentration in the inactivation of cytochrome P-450 in microsomes in a phosphate buffer at pH 7.3.[64]

Systematic studies of the interactions of various detergents in an aqueous medium with myoglobin and cytochromes c and P-450 have been carried out in our laboratory.[60] These proteins differ not only in solubility and molecular weight but also in the strength of binding of haem to the apoprotein. The detergents employed were the zwitter-ionic surfactant 1-(N-$C_{12}H_{25}$-NN-dimethylamino)propane-3-sulphonate (TM 3-12) and the non-ionic surfactants Twin 20 and Triton N-101, belonging to type A, which embraces amphiphilic compounds exhibiting lyotropic mesomorphism and forming spherical or ellipsoidal micelles in an aqueous medium.[119] We also used sodium cholate, which belongs to the group of charged detergents of type B, differing by the absence of lyotropic mesomorphism and forming aggregates in an aqueous medium containing from 2 to 8 surfactant molecules.[119] The interaction of the haemoprotein enumerated above with detergents of both types is accompanied by a decrease of the intensity of the Soret bands in the absorption spectra. The rate of this process is determined by the nature of the detergents, their concentration, and temperature and is a maximum for the zwitter-ionic surfactant TM 3-12. The rate constants for the transformation of the haemoproteins depend in a complex manner on the detergent concentrations. Their influence on the secondary structure and conformation of proteins, leading to the loss of haem, has been demonstrated by the CD method and the method involving the second derivatives of the absorption spectra of haemoproteins in the presence of detergents. In conformity with the model proposed for the interaction of detergents with haemoproteins, the process takes place at two levels—molecular and supermolecular.[60] At detergent concentrations below the critical concentration for micelle formation, a bimolecular interaction of the surfactants with the proteins is observed; above this concentration, not only surfactant molecules but also their micelles (type A) or associated species (type B) interact with the proteins. The molecular mechanism of the interaction of surfactants with proteins consist in the fact that the surfactant molecules penetrate via their hydrophobic fragments into the cavities and "cracks" in the protein molecules, making more hydrophobic the regions adjoining the aromatic aminoacids, which is confirmed by the increase of the amplitude of the second derivatives in the absorption spectra of cytochrome c and P-450 LM-2 following the addition of Twin 20 and TM 3–12.[60] Not only does the hydrophilic–hydrophobic balance change within the protein globule but also the secondary protein structures break down, which is confirmed by CD spectra, reflecting the decrease of the content of the α-helix sections in myoglobin molecules after the addition of TM 3–13.[60] The zwitter-ionic surfactant TM 3–12 interacts most strongly with proteins. The effect of surfactants on haemoprotein leads to conformational changes in the protein, facilitating the loss of haem. The transformation of myoglobin in the presence of detergents of different types takes place with $E_{act} = 17–23$ kcal mol^{-1}, which can be attributed to the dissociation of the haem iron–histidine nitrogen coordinate bond.[60] Individual detergents and their mixtures increase or decrease the values of ΔH^* for the transformation of myoglobin. A relation (compensation effect) is observed between ΔH^* and ΔS^*, which is described by the equation $\Delta H^* = A + \beta\Delta S^*$, where $A = 22\,000$ cal mol^{-1} and $\beta = 300$ K. The coefficient β should usually be close to the average experimental temperature, which has in fact been observed in the present case: $T_{av} \cong \beta = 300$ K.

Inverted surfactant micelles in organic solvents which have solubilised the proteins constitute a special case. Proteins are almost insoluble in pure organic solvents. In order to increase their solubility, certain surfactants are employed. In contrast to aqueous solutions, in the inverted micelles the detergents interact with proteins mainly via polar fragments. A mixed solvation shell consisting of surfactant molecules, the organic solvent, and water is formed around the protein globule. The composition of the solvation shell and the ratio of the components in the micellar solution influence directly the stability and activity of the proteins in the system. The reader can obtain exhaustive information about the functioning and properties of the proteins in these systems from a number of reviews.[83–85,121]

V. TEMPERATURE DEPENDENCE OF THE RATE CONSTANTS FOR THE INACTIVATION OF ENZYMES AND THE PHYSICOCHEMICAL SIGNIFICANCE OF THE THERMODYNAMIC ACTIVATION PARAMETERS FOR THIS PROCESS

The temperature variation of the rate constants for the inactivation of enzymes is described by the Arrhenius equation and is characterised by a single value of E_{act} only if the enzymes have been studied in highly dilute solutions. Only one E_{act} is characteristic of dilute solutions of monomeric lysozyme[47] and subunit lactate and malate dehydrogenases.[58,59] An increase of the protein concentration in solution leads to the appearance of breaks in the Arrhenius plots (Fig.4), since the constants k_{in} depend on the initial protein concentration and other parameters.[47,58,69] In all cases, when the initial protein concentration has been chosen arbitrarily, there are breaks in the Arrhenius plots reflecting changes in the rate constants for the inactivation of enzymes in concentrated solution. For membrane proteins, there are other causes which explain the presence of breaks in the Arrhenius plots: firstly, the conformation and stability of the proteins in the membrane depend on the effect, nature, and physical properties of the surrounding lipids, whose phase transitions induce an abrupt change in E_{act} in the thermal transformation of the protein;[82,90,113,114] secondly, at certain temperatures there is a possibility of "phase" transitions in the protein itself, leading to a sharp change of its conformation[41–44,122] and hence to a change in E_{act} for the thermal degradation process; thirdly, there is a possibility of the existence of different conformers of the same form of the biocatalyst, which are characterised by different E_{act} for the thermal denaturation process. All the possibilities listed above can be realised not only in biomembranes but also in liposomes[123,124] and possibly in inverted surfactant micelles.

Clearly the rate constants for the inactivation of proteins determined in highly dilute aqueous solutions are closest to their true values, because in this case the possibility of the association of the monomeric proteins and of the reassociation of the subunits of oligomeric enzymes is reduced to a minimum. It is therefore useful to consider E_{act} on the activation characteristics ΔH^* and ΔS^* obtained with the aid of the Arrhenius–Eyring equation (1) in the first place for those proteins whose inactivation has been characterised by the rate constants k_0 for their dilute solutions. Under such conditions, we investigated three enzymes–lysozyme,[47] malate dehydrogenase,[59] and lactate dehydrogenase.[58] It follows from the Arrhenius equations (8), (11), and (12) that only in the case of lysozyme [Eqn.(8)] is the pre-exponential factor for the rate constant close to its limiting value for unimolecular reactions.[6,52] For two subunit enzymes, the pre-exponential factor exceeds by many orders of magnitude the typical factors in the equation for unimolecular reaction rate constants (10^{10}–10^{11} s^{-1}) and corresponds to a high activation entropy (Table 1). This is not unexpected, because it has already been known for a long time that the inactivation of proteins is characterised by high values of ΔH^* and ΔS^*.[6–8,10,11,23,125]

In applying the Arrhenius–Eyring equation (1) to the transformations of enzymes and enzymic reactions, one must remember that, as a consequence of the non-elementary nature of these processes, the parameters determined from the temperature variation of k_{in} for enzymes and the rate constants for the enzymic reactions are always real quantities reflecting the entire complexity of the macrostage being characterised—the presence of microstages, which are not outwardly manifested, the influence of the solvent and the environment of the enzyme, etc.[8] (pp.175–185). For this reason, in the analysis of the thermodynamic and kinetic parameters of the inactivation of enzymes, it is essential to resort to additional considerations based on the theory of chemical kinetics and empirical data for simpler chemical and model systems and also to the results of the study of the enzyme inactivation processes by NMR and CD spectroscopic and densitometric methods, sedimentation analysis, etc.

As regards kinetic data, Likhtenshtein proposed three types of methods for their analysis in the case of enzymic processes:[8] (1) quantitative comparison of the energetic and entropic parameters for enzymic and model reactions; (2) theoretical estimation of the parameters for different versions of the mechanism of the reactions investigated; (3) correlation between the energetic and entropic parameters of enzymic processes (compensation effect). Since the present level of the theory does not allow the calculation of the absolute values of the energies and entropies of activation for reactions in a condensed phase, the third type of analysis of enzymic processes is of great interest, particularly when one is dealing with series of reactions, with the specific alteration of one of the parameters keeping the others constant, or with changes in the conditions of a process involving the same enzyme.

The correlation between the energetic and entropic parameters in an enzymic process was first noted by Doherty and Vaslow.[126] On changing the pH, the authors observed parallel compensating changes in the parameters ΔH and ΔS

in the binding of the substrate to α-chymotrypsin. Since then, numerous data concerning the compensating changes in ΔH and ΔS (ΔH^* and ΔS^*) in a wide variety of enzymic processes have been published. These data have been examined in detail and analysed in a series of investigations.[8,11,12,125–130] The survey of the available information about the inactivation of proteins shows that the principal kinetic characteristics of this process are as follows: (1) sharp changes in the rates of inactivation are observed within a fairly narrow temperature range or within narrow ranges of concentrations of hydrogen ions, organic solvents, and other additives; (2) the inactivation is characterised by anomalously large (compared with the parameters of the usual chemical reactions) values of E_{act} and ΔS^*, which reach 180 kcal mol^{-1} and 600 e.u. per mole of the protein in some cases (see Table 1 and also the compilations of data in Refs. 3, 6, 7–11, 22, 23, and 125); (3) the values of E_{act} and ΔS^* are extremely sensitive to changes in the conditions within the medium (pH, ionic strength, nature of the buffer, the presence of stabilising additives, the introduction of proteins into micelles, liposomes, and gels, etc.); (4) there is a linear relation between the experimental values of E_{act} and the activation entropy for different proteins and for the same protein under different conditions, expressed by the equation[131,132] $E_{act} = \alpha + \beta\Delta S^*$.

It follows from the numerous data discussed previously and quoted in this review that, on passing from one protein to another and also on changing the pH and the concentration of ions and denaturing additives, the activation energy and entropy almost always change in parallel (see, for example, Fig.11). The slope of the linear plots of E_{act} against ΔS^* is known to be the same as the slope of the linear plots of the reversible inactivation parameters ΔH and ΔS.[7–10,22,125] The kinetic and thermodynamic compensation effects are characterised by similar coefficients β and identical scales of the changes in the energetic and entropic parameters.[8,125]

In conformity with existing ideas, the processes involving the inactivation (denaturation) of biopolymers are cooperative conformational transitions. The thermodynamic theory of cooperative systems has been developed in a number of studies in relation to biopolymers.[133–137] Denaturation is sometimes regarded as a "fusion" process, although in the case of proteins one can speak of analogies with fusion processes and "phase" transitions only approximately, since proteins are regarded as "aperiodic" irregular crystals, characterised by differences between the energies of the cooperative linkage and by defects in various parts of large molecules. The cooperative processes in proteins are intermediate between the usual chemical reactions, in which a small number of molecules participate, and large-scale phase transitions with participation of an enormous number of identical species.[8] We shall not consider here the different kinetic models of the conformational transitions in proteins, since they have been analysed in detail in monographs and reviews.[8,10,125,133–137]

According to Privalov,[138] there is at present no doubt about the energetic discreteness of proteins, which reflects their structural discreteness, since proteins are complex systems consisting of more or less independent but fully defined cooperative subsystems. The subdivision of the macromolecule into cooperative subsystems (domains) is a general principle of the structural organisation of protein molecules, which has evolutionary, functional, and physical bases. E_{act} and the activation characteristics ΔH^*, ΔS^*, and ΔG^* for the thermal inactivation (denaturation) of proteins therefore refer to complex cooperative **rearrangements** of a part of the protein molecule and of its immediate environment. The question arises whether it is possible to refer in some cases the characteristics listed above to a rigorously defined molecular stage in the inactivation of the protein. The set of kinetic,[47] thermodynamic,[41] spectroscopic,[42,45,46] and ^{13}C NMR data[43] obtained for the inactivation of lysozyme permits the claim that this process begins with the ionisation of the Glu-35 residue, which destabilises the adjoining section of lysozymes and causes the breakdown of its α-helix structure in the region of the active centre. Thus, even in this comparatively simple object, which has been characterised in detail, the rate-limiting step in the irreversible inactivation is accompanied by complex conformational changes, which are reflected quantitatively by the values of E_{act}, ΔH^*, and ΔS^*.[47] A second example of a protein for which one can speak quite definitely about the elementary inactivation stage is cytochrome P-450. The loss of catalytic activity by this protein is associated with the increase of the length and rupture of the coordinate bond between the haem iron and the sulphur atom of the cysteine residue.[50,82,88,90] However, a change in the conformation of the apoprotein precedes this step, i.e. in this case the rate-limiting stage in the activation process is associated with marked conformational changes in the biocatalyst, which is reflected by the thermodynamic and activation characteristics of the process.[50,64,65]

The question arises in what cases is it legitimate to calculate the activation characteristics of the thermal inactivation of proteins from the temperature variation of k_{in}, the effective character of which is known beforehand. We believe that this can be usefully done only when one is dealing with a comparison of the behaviour of the same enzyme under the influence of different agents, a comparison of different enzymes acted upon by the same agent under identical conditions, or the modification of the enzyme by various agents under the same conditions. There is no point in discussing the absolute values of E_{act}, ΔS^* and ΔG^* in such cases, since only the character of the variation of these quantities when a specific parameter is varied and all the remaining parameters are kept constant, and not the values themselves, carries information. Thus analysis of the activation characteristics obtained reduces to the discussion of the compensation states between their energetic and entropic components.[7,8,11,125,127–132]

In discussing the enthalpy–entropy compensation in the inactivation (denaturation) of proteins, one should remember that there is a doubt about its existence as an independent physical phenomenon.[9] It has been claimed that, in all enzymic reactions exhibiting the enthalpy–entropy compensation, a key role is played by the solvent (liquid water), which is a constant participant in all physiological processes and constitutes a natural inexhaustible reservoir of chemical free energy in living nature.[125,129] The conformational rearrangement in proteins and the changes in their interactions with water molecules which they entail alter significantly the structure of the entire mass of liquid water. This factor and also the very narrow range of independent parameters (pH, temperature, and the salt composition of the medium), which determine the conditions of the enzymic process, lead to the appearance of trivial linear relations between the enthalpy and entropy changes.[125,129]

Blyumenfel'd[9] quite justifiably assumes that the enthalpy–entropy relations do not reflect any special essential physical features of the reactions and are a simple consequence of the general laws of equilibrium thermodynamics and may not exist at all if the equilibrium thermodynamic process ($\Delta G \cong$ const.) occurs within a very narrow range of variation of an independent variable (temperature, hydrogen ion concentration, etc.). In the study of the reactions of biopolymers, where equilibrium statistical dynamics is applicable only subject to major stipulations, any kind of serious analysis of compensation relations frequently lacks physicochemical significance.

VI. CONCLUSION

It follows from numerous experimental data that the thermal inactivation of enzymes is a complex process consisting of several consecutive-parallel stages and therefore it frequently cannot be described in terms of the first order kinetic law. As a rule, the semilogarithmic forms of kinetic curves have breaks or are altogether non-linear. Even in those cases where a first-order equation describes satisfactorily the kinetic data, the effective inactivation rate constant k_{in} depends on the initial protein concentration.

Two approaches have been proposed to achieve a rapid and correct quantitative characterisation of the process leading to the thermal inactivation of proteins. One of them has been used by Poltorak and co-workers;[24-32] the thermal inactivation scheme is described by equations which have been solved by approximate methods permitting the determination of the rate constants for the first reversible and second irreversible stages and the calculation of the equilibrium constant between the native and reversibly inactivated forms of the proteins. This method permits a quantitative description of the kinetic curves for the thermal inactivation of monomeric and subunit proteins at an arbitrarily selected initial concentration of the latter.

The second method has been used in a series of our own investigations[47,58,59,70] and consists in plotting kinetic inactivation curves for different initial protein concentrations, their linearisation in terms of a first order equation, the determination of the dependence of k_{in} on the protein concentration, and the calculation of the rate constant k_0 at infinite dilution of the protein. We believe that the rate constant k_0 is the most correct quantitative characteristic of the thermal inactivation of proteins. The disadvantages of our method are the approximate character of the equations relating k_{in} to the initial protein concentration and the difficulties in assigning a physicochemical significance to the coefficients α and γ in these equations [see Eqns.(9) and (10)]. An advantage of the method is the fact that we obtain the rate constant for infinitely dilute solutions and hence can apply the equations of classical thermodynamics in the analysis of the temperature variation of these constants. The temperature variation of k_0 is described by the Arrhenius equation, while $k_{in}-1/T$ plots are complicated by breaks and the interpretation of these relations altogether lacks physicochemical significance.

One should recall that the thermodynamic activation parameters (ΔH^*, ΔS^*, and ΔG^*), obtained from the analysis of the temperature variation of k_0, cannot be referred to a single rigorously defined molecular stage in the thermal inactivation of proteins, because they always characterise a complex cooperative process involving conformational transformations in the biopolymer. This is the main cause of the difference between these quantities and the activation parameters for the thermolysis of low-molecular-weight chemical compounds.

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Methods for the Theoretical Description of the Energy of Resolvation of Ions

V.S.Markin and A.G.Volkov

Present-day theories of ion solvation have been examined. The experimental values of the standard free energies of resolvation and the standard redistribution potentials of ions between water and organic solvents have been given. The contribution of dielectric saturation to the electrostatic component of the free energy of resolvation has been analysed. The results of theoretical calculations have been compared with the experimental dependence of the standard free energy of solvation on the static and optical dielectric constants of the solvents, and also on the size of the ions. The solvophobic contribution to the energy of resolvation has been estimated.
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I. INTRODUCTION

In recent years there has been a sharp increase in interest in the experimental and theoretical determination of the values of the standard free energy of resolvation of ions. A knowledge of these quantities is required in the study of the electrochemistry of the interface between two immiscible electrolyte solutions,[1-5] the transport of ions through biological and synthetic membranes,[6] the mechanisms of interphase and surface catalysis,[7-10] the kinetics of charge transfer through an oil–water interface,[11-13] the coupling of heterogeneous reactions in bioenergetics,[5] extraction,[14] and the production of ion-selective electrodes.[15]

The term solvation refers to all the energetic and structure changes taking place in a system in the transfer of ions from the gas phase to the liquid phase of a solvent. The interaction of an ion with a solvent includes several effects: 1) electric polarisation of the medium; 2) the production in the medium of a cavity to accommodate the ion; 3) a change in the structure of the solvent, involving the breakdown of the old structure and the production of a new structure close to the ion (the formation of cavities and the change in the structure of the solvent close to the ion are sometimes combined in a single effect, called the solvophobic or hydrophobic effect); and 4) specific interaction of the ions with the solvent molecules (the formation of hydrogen bonds, donor–acceptor interaction), etc. This division is to some extent arbitrary, since different effects may overlap; for example, the electric polarisation of a solution may have a significant influence on its structure. It is possible, however, to carry out the theoretical calculation of individual effects.[16]

In the present review, present-day theories of ion solvation will be characterised briefly. To find the standard free energy of resolvation $\Delta^{\alpha}_{\beta}G^0_i$ of an ion i, the Gibbs free energies of the ion in two media, α and β, are compared. If the phase β is a vacuum, the quantity

$$\Delta^{\alpha}_{\text{vac}}G^0_i = G^{0,\alpha}_i - G^{0,\text{vac}}_i$$

is called the energy of solvation of the ion i in the phase α. The energy of resolvation can obviously be represented as the difference between two solvation energies:

$$\Delta^{\alpha}_{\beta}G^0_i = \Delta^{\alpha}_{\text{vac}}G^0_i - \Delta^{\beta}_{\text{vac}}G^0_i. \tag{1}$$

The standard free energies of resolvation of ions from water into different organic solvents are found by cyclic voltammetry, chronopotentiometry, polarography, data on the spin–lattice relaxation of the quadrupole moments of the nuclei of the ions, and also from solubility and extraction data.[1,12,14,17–30] These quantities are given in Table 1, which shows that the standard free energy of resolvation of ions depends markedly on the nature of the ion and the solvent.

Figs. 1 and 2 give the dependence of the energy of resolvation on the static and optical dielectric constants of non-aqueous solvents. Fig. 3 gives the dependence of the standard free energy of hydration on the radius of the ion. Figs. 1–3 and Table 1 show that the energy of resolvation (and hydration) decreases sharply with increase in the size of the ion and the static and optical dielectric constants of the medium.

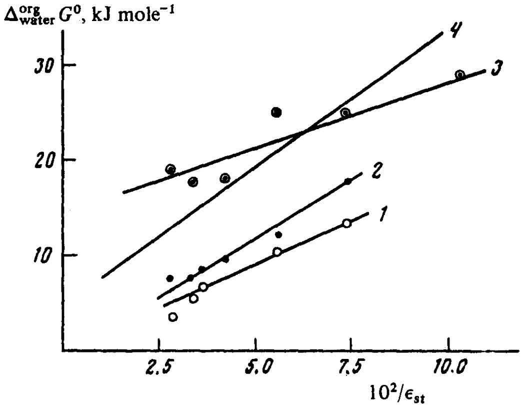

Figure 1. Dependence of the standard free energy of resolvation on the static dielectric constant of the non-aqueous phase; curves *1* (Me_4N^+), *2* (ClO_4^-), and *3* (I^-) give the experimental data from Table 1, and curve *4* gives the results of the calculation using the Born equation for Me_4N^+.

Table 1. Standard free energies of resolvation of the ions $\Delta^{\text{org}}_{\text{water}}G^0_i$ (kJ mole^{-1}) and distribution potentials $\Delta^{\text{org}}_{\text{water}}\phi^0$ (mV) of the ions between water and organic solvents at 298 K.[12,14,17–30]

Ion	Nitrobenzene		Acetophenone		Isobutyl methyl ketone		1,2-Dichloroethane		1,1-Dichloroethane		Dichloromethane	
	$\Delta^{\text{org}}_{\text{water}}G^0_i$	$\Delta^{\text{org}}_{\text{water}}\varphi^0_i$	$\Delta^{\text{org}}_{\text{water}}G^0_i$	$\Delta^{\text{org}}_{\text{water}}\varphi^0_i$	$\Delta^{\text{org}}_{\text{water}}G^0_i$	$\Delta^{\text{org}}_{\text{water}}\varphi^0_i$	$\Delta^{\text{org}}_{\text{water}}G^0_i$	$\Delta^{\text{org}}_{\text{water}}\varphi^0_i$	$\Delta^{\text{org}}_{\text{water}}G^0_i$	$\Delta^{\text{org}}_{\text{water}}\varphi^0_i$	$\Delta^{\text{org}}_{\text{water}}G^0_i$	$\Delta^{\text{org}}_{\text{water}}\varphi^0_i$
Li^+	38.4	−398	—	—	20.3	210	—	—	—	—	—	—
Mg^{2+}	71.4	−370	—	—	—	—	—	—	—	—	—	—
Na^+	34.5	−358	—	—	—	—	—	—	28.9	−299	—	—
Ca^{2+}	68.3	−354	—	—	—	—	—	—	—	—	—	—
Sr^{2+}	67.2	−348	—	—	—	—	—	—	—	—	—	—
H^+	32.5	−337	—	—	—	—	—	—	—	—	—	—
Ba^{2+}	63.3	−328	—	—	—	—	—	—	—	—	—	—
NH^+	27.4	−284	—	—	—	—	—	—	—	—	—	—
K^+	24.3	−252	—	—	—	—	—	—	29.7	−307	—	—
Rb^+	19.9	−206	—	—	—	—	—	—	28.9	−299	—	—
Cs^+	15.5	−161	—	—	—	—	17.9	−185	—	—	—	—
$(Me)_4N^+$	3.4	−35	—	—	—	—	17.6	−182	17.5	−181	18.8	−195
$(Et)_4N^+$	−5.8	60	—	—	8.7	−90	4.2	−44	10.8	−112	4.2	−44
$(Pr)_4N^+$	−15.5	161	—	—	—	—	−8.8	91	−2.2	23	−8.8	91
$(But)_4N^+$	−24.2	248 * [27]	−15.6	162	−19.3	200	−21.8	226	−11.7	121	−22.2	230
$(Ph)_4As^+$	−35.9	372	−16.2	168	—	—	−35.2	365	−27.3	283	—	—
Cl^-	30.5	316	—	—	50.2	520	46.5	481	57.8	600	46.4	481
Br^-	28.5	295	—	—	—	—	38.5	399	42.5	440	39.3	408
I^-	18.8	195	12.4	128	—	—	26.4	274	30.6	317	26.4	273
ClO_4^-	8.0	83	1.8	19	—	—	17.2	178	22.4	232	21.3	221
2,4-DNP$^-$	7.3	76	—	—	—	—	—	—	—	—	—	—
Pi^-	−4.5	−48	—	—	11.6	120	—	—	—	—	−6.7	−69
$(Ph)_4B^-$	−35.9	−372	−16.2	−168	—	—	−35.2	−365	−27.3	−283	—	—
DCC^-	−50.2	−520	—	—	—	—	—	—	—	—	—	—
SCN^-	16.0	176	11.0	144	—	—	25.5	264	—	—	—	—
IO_4^-	6.9	75	1.5	15	—	—	14.5	159	—	—	—	—
ClO_3^-	—	—	19.3	200	—	—	33.1	343	—	—	—	—
NO_3^-	24.4	253	20.4	211	—	—	33.9	351	—	—	—	—
BF_4^-	11.0	121	—	—	—	—	17.9	197	—	—	—	—

Note: $(Alk)_4N^+$ = tetra-alkylammonium, DCC^- = dicarbollylcobaltate, DNP^- = dinitrophenolate, Pi^- = picrate.
* 255 mV,[20] 275 mV.[26]

The standard free energies of resolvation of ions, obtained by different methods, do not always coincide exactly with one another. These quantities can be calculated or measured by two methods. It is possible to determine the energy of solvation of the ion in the two pure solvents α and β, and then to use Eqn.(1) to find the standard free energy of the transfer of the ion i from the solvent β to the solvent α. If two immiscible liquids α and β are in contact and in equilibrium, some solvent from each of these phases dissolves in the other phase. In this case the phases α and β will be mutually saturated. The corresponding energy of resolvation of the ion on its transfer between the two equilibrated solvents is called the standard free energy of distribution.[22] For most known ions and solvents, the standard free energies of transfer and distribution coincide with one another within the limits of accuracy of the measurements. It is not excluded, however, that for some solvents and ions these quantities differ.

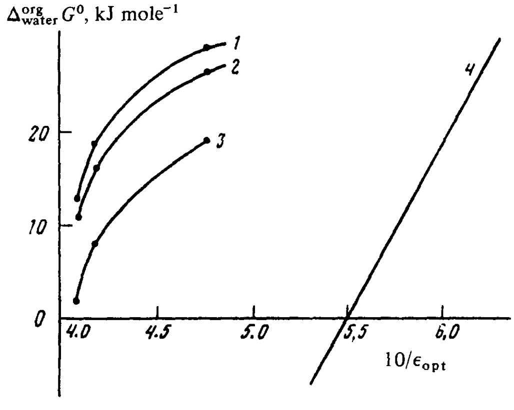

Figure 2. Dependence of the standard free energy of resolvation of the ions on the optical dielectric constant of the non-aqueous phase: curves *1* (I^-), *2* (SCN^-), and *3* (ClO_4^-) give the experimental data from Table 1, and curve *4* gives the results of the calculation using the Born equation for I^-, assuming that $\varepsilon = \varepsilon_{\rm opt}$; the values of the optical dielectric constant were taken from Table 2.

Thus in the analysis and application of the values of the standard free energy of resolvation it is necessary to consider whether ion transfer takes place between the pure solvents or between the mutually saturated solvents.

II. ELECTRIC CONTRIBUTION TO THE SOLVATION ENERGY

There are two groups of models for calculating the electric component of the solvation energy. In the first group the medium is regarded as a structureless continuum, and in the second as a set of individual particles with real or simplified properties. In early work, the structure of the solvent was taken into account by calculating directly the energies of specific configurations of the solvent molecules close to the ion; the actual configuration and the number of molecules included in it were selected somewhat arbitrarily from various physical considerations, to give agreement between the calculated and experimental data. In these models, the statistical properties of the solution, which are undoubtedly important for a correct description of the phenomenon of solvation, were ignored completely. The modern approach involves the development of a statistical theory of the ion–dipole plasma, reflecting both the energetic and statistical aspects of the phenomenon.

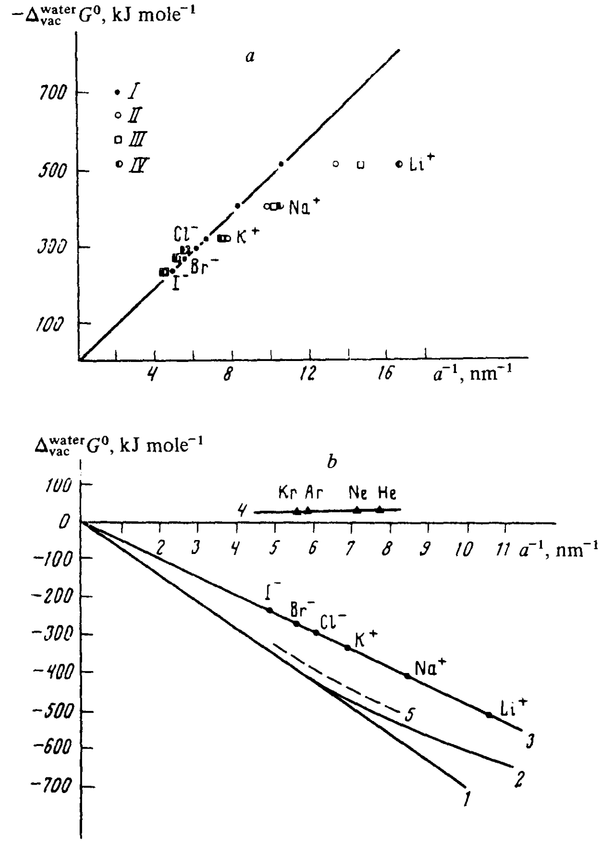

Figure 3. Dependence of the standard free energy of hydration of inorganic ions on their radius; the ionic radii were those of Gourary and Adrian (I),[31] Waddington (II),[37] Goldschmidt (III),[36] and Pauling (IV);[35] *a*: experimental data from Refs.29 and 30; *b*: *1*) calculated using the Born equation, *2*) calculated with allowance for dielectric saturation,[2] *3*) experimental data from Refs.29 and 30, *4*) standard free energies of solution of the inert gases (1 atm in the gas phase and a mole fraction of 1 in the aqueous solution at 298 K), *5*) sum of curves *2* and *4*.[2]

There is also an intermediate approach, in which, while remaining within the framework of continuum theories, attempts are made to take account of the influence of the discrete nature of the solvent on the effective parameters of the model. For this purpose, account is taken of non-linear dielectric effects, and the mutual correlation of the polarisation vectors of the solvent molecules, situated at short distances from one another, is analysed using the theory of non-local electrostatics. Each of these approaches, reflecting the role of different effects, has its own advantages.

1. The Born Model

In the first continuum model, developed by Born,[32] the ion was regarded as a solid sphere with a given radius a, immersed in a continuous medium with a constant dielectric constant ε (Fig.4a). This was a macroscopic theory, which described the properties of the solvent at short distances from the ion by macroscopic laws. The energy of solvation (more accurately, its electric part), calculated for one particle, is given according to the Born theory by the familiar equation

$$\Delta_{\text{vac}}^{\alpha} G^0(\text{el}) = -\frac{z^2 e_0^2}{8\pi\varepsilon_0 a}\left(1-\frac{1}{\varepsilon^{\alpha}}\right) \tag{2}$$

where ε_0 is the electric constant, ε^{α} the dielectric constant of the medium, z the charge number of the ion, and e_0 the charge of the electron. From this equation, the energy of resolvation when an ion is transferred from the medium α to the medium β (that is the difference between the energies in the media β and α) is given by:

$$\Delta_{\alpha}^{\beta} G^0(\text{el}) = -\frac{z^2 e_0^2}{8\pi\varepsilon_0 a}\left(\frac{1}{\varepsilon^{\alpha}}-\frac{1}{\varepsilon^{\beta}}\right) \tag{3}$$

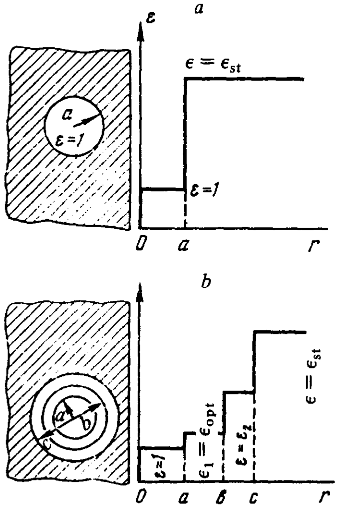

Figure 4. Models of Born (a) and Abraham and Liszi (b).[49,50]

Calculations using the Born equation give values of the solvation energy differing considerably from the experimental values.[2,33,34] Since the energy of resolvation is often the small difference between two comparatively large solvation energies, a relatively small uncertainty in the determination of each of these quantities may lead to a considerable overall uncertainty, even an incorrect sign. For example, it follows from Eqn.(3) that for $\varepsilon^{\alpha} > \varepsilon^{\beta}$, it is more favourable for the ion to be in the solvent α, irrespective of its actual size. This is not always observed experimentally, however. Small ions with a radius $a < 0.2$ nm are in fact found chiefly in a polar solvent with a high dielectric constant, but at the same time, large organic ions often enter the hydrophobic phase preferentially.

Distribution coefficients[1,14,17] and extraction, solubility[14,17] and voltammetric data[12,22,26] indicate that the standard free energy of the transfer of an ion from water to a less polar solvent is positive for ions with a small radius, and negative for ions with a large radius, whereas according to Eqn.(3) it is a constant-sign function of the radius.

Born's equation gives values of the solvation energy which are too high (too negative) (Figs.1 and 3). When comparing specific values with experimental data, it is necessary to assign a radius to each ion. This procedure is to some extent arbitrary, since the ionic radius is only an effective parameter, the use of which makes possible the most successful description of various properties of ionic systems. It is often found that different properties of a system require the choice of different ionic radii for their description. It is pointless to raise the question of which value of the ionic radius is correct, and which is not, although naturally there are reasonable physical restrictions on the range within which the value of the effective radius of an ion may lie.

This is reflected in the fact that there are at least four scales of ionic radii, namely those of Pauling,[35] Goldschmidt,[36] Waddington,[37] and Gourary and Adrian,[31] calculated on the basis of different assumptions. The first three scales differ little from one another, but the fourth differs from the others. Blandamer and Symons[38] tried to select the most successful scale of ionic radii by comparing thermodynamic data on the Gibbs free energy and entropy of hydration of the ions. They showed that if any of these quantities is plotted as a function of $1/a^2$, all the points corresponding to the alkali metal cations and the halide anions lie on the same smooth curve if the Gourary–Adrian radii are used. The other sets of radii give two different curves, one for the cations and another for the anions. It is difficult to say what importance should be given to the observed regularity, since as yet it has no theoretical foundation.

Since Born's equation (2) gives the dependence of the solvation energy on $1/a$, the same coordinates are used in Fig.3. Fig.3a gives the experimental data for six cations and anions on all four ionic radius scales. The data on the Gourary–Adrian scale lie ideally on one straight line, confirming the observation made in Ref.38. This fact undoubtedly deserves attention. The data using the other scales deviate from this straight line, although a significant deviation is observed only for the small ions Li^+, Na^+, and K^+, and the points for Cl^-, Br^-, and I^- deviate little. The experimental points are compared with the theoretical predictions in Fig.3b. To avoid overloading the Figure, the experimental points are given only on the Gourary–Adrian scale (curve *3*). The non-electrostatic part of the free energy of hydration is given by curve *4*.

Different independent methods can be used to determine the hydration energy of the inert gases. If the radii of the ions and atoms of the inert gases coincide, the free energy of solution of the gas is simply the non-electrostatic component of the free energy of hydration.

The electrostatic part of the hydration energy, calculated from the Born equation, is given by curve *1* in Fig.3b. It in fact is greater (by ~50%) than the experimental values. It may be noted that it is necessary to compare with experiment the sum of curves *1* and *4*; this improves the situation, but only very slightly. The sum of the electrostatic and non-electrostatic parts of the free energy of hydration corresponds to curve *5*; the values of the sum are in fact close to the experimental points. The discrepancy between theory and experiment is smallest when the Gourary–Adrian scale of ionic radii is used.

Thus the Born theory requires improvement. Eqn.(2) contains only two experimental parameters, the ionic radius a and the dielectric constant ε. In principle, it is possible to achieve satisfactory agreement between theory and experiment by changing either of these quantities in appropriate fashion. This formal fitting of the parameters, however, leads to physically unreasonable values of a and ε, which do not lie on any one acceptable scale. Thus although this fitting gives an empirical equation showing good agreement with experiment, it cannot give a physical explanation of the phenomenon of solvation.

The use of ideas on the dielectric saturation of the medium in the field of the ion are more attractive from this viewpoint.[2,39–52] Allowance for this effect decreases the absolute magnitude of the electric component of the solvation energy. Again, formally, it is possible to achieve very good agreement between theory and experiment by selecting suitable saturation range dimensions and dielectric constant values. Ideal agreement was obtained in this way by Abraham and Liszi's group.[47–52] There still remains the question, however, of whether these results give a physical explanation of the phenomenon of solvation, or only a successful empirical equation, convenient for practical applications. Since published views on the role of saturation effects in the solvation of ions are contradictory, this question will be examined specially.

2. Non-linear Dielectric Effects

The simplest approach to the calculation of the electrostatic part of the solvation energy, based on the continuum description, and methods for its improvement by taking account of the dielectric saturation of the medium in the field of the ion, can be considered. Some time ago, it appeared that this problem had been sufficiently elucidated; allowance for dielectric saturation gave too small a correction to the Born theory.[17,18] In recent years, however, interest has again been shown in this problem.[2,47–52] Allowance for dielectric saturation gave new results, which unlike the previous results show ideal agreement with experimental data.[47–52] An attempt has been made to analyse the situation that has arisen and to propose simple equations for estimating the effect of dielectric saturation and its role in the phenomenon of ion resolvation.

One method of improving the Born theory is by taking account of non-linear dielectric effects. The dielectric constant of a medium containing polar molecules should change with change in the intensity of the external electric field. This is due both to breakdown of the actual structure of the associated dipoles and to dielectric saturation.[39–41]

A theoretical analysis of the properties of water[42] within the framework of the model used by the author showed that when an electric field is applied, the dielectric constant of water may decrease from the static value $\varepsilon_{st} \cong 80$ to the optical value, equal to the square of the refractive index, that is $\varepsilon_{opt} = 1.8$. Saturation is reached in fields whose intensity exceeds 10^9 V m^{-1}. Because of technical difficulties, it has been possible to verify the theory only in fields with an intensity not exceeding 2×10^7 V m^{-1}, where the decrease in the dielectric constant did not exceed 1% (Fig.5). A detailed discussion of this question can be found in Refs. 43–45.

The first attempt to take account of the dielectric saturation of the medium close to the ion in the calculation of the solvation energy was made in 1926.[46] Introduction of the corresponding correction makes it possible to move the calculated values obtained using the Born theory in the required direction. Subsequently, attempts to attribute the difference between the experimental values of $\Delta^{\alpha}_{\text{vac}}G^0$ and the values calculated using the Born theory entirely to dielectric saturation raised serious objections.[33,34]

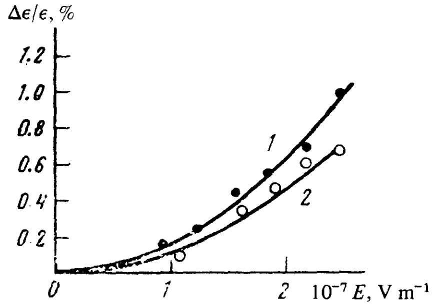

Figure 5. Influence of the intensity of the electric field E on the dielectric constant of nitrobenzene (1) and water (2);[40,41] $\Delta\varepsilon = \varepsilon_{st} - \varepsilon(E)$.

The density of the free energy of the electric field in a dielectric in the general case is described by the integral

$$g(\mathrm{r}) = \int_0^{\mathrm{D}} \mathrm{E}\,d\mathrm{D} \tag{4}$$

where $\mathbf{E}$ is the intensity of the electric field, and $\mathbf{D}$ the electric induction. In weak fields with a linear relationship $\mathbf{D} = \varepsilon_0\varepsilon\mathbf{E}$, integration of the density of the free energy (4) over the whole of space outside the ion leads to the Born equation (2).

In the general case, the electric induction can be represented as follows:[42]

$$D = \epsilon_0\epsilon_{opt}E + N\mu L(E) \tag{5}$$

where

$$\mu = \frac{\epsilon_{opt} + 2}{3}\mu_0\tilde{g}^{1/2} \tag{6}$$

N is the number of molecules of the dielectric in unit volume, μ_0 their dipole moment in a vacuum, and $\tilde{g}^{1/2}$ the Kirkwood factor, which depends on the field and takes account of the associated character of the dipolar molecules (in a non-associated liquid and in high fields, $\tilde{g} = 1$). For the function $L(E)$ it is usual to employ the Langevin model function, but to estimate the effect it is sufficient to know the dependence of D on E in the most general form. From general physical considerations it is clear that with increase in E the function $L(E)$ should increase and tend to a limiting value of 1. As a result, the dependence of D on E moves from one limiting law to another. At low intensities

$$D \cong [\epsilon_0\epsilon_{opt} + N\mu(L'|_{E=0})]E = \epsilon_0\epsilon_{opt}E \tag{7}$$

and at high intensities

$$D \cong \epsilon_0\epsilon_{opt}E + N\mu. \tag{8}$$

On the graph giving the dependence of E on D (Fig.6), the straight line ac corresponds to the linear function. As saturation takes place, the curve begins to rise steeply, reaching another asymptote be. The density of the free energy in the linear approximation is equal to the area of the triangle *acd*, and the value of the total integral (4) is equal to the much larger area of the curvilinear triangle *abd*. The difference between these values arises when the electric induction D is greater than the characteristic value D_{sat}, which can readily be shown to be equal to

$$D_{\text{sat}} = N\mu. \tag{9}$$

Since the electric induction in a spherically symmetrical field is independent of the dielectric constant

$$D = \frac{ze_0}{4\pi r^2} \tag{10}$$

it is possible to indicate the characteristic distance from the centre of the ion, within which the saturation effect has an influence:

$$r_{\text{sat}} = \left(\frac{|z|e_0}{4\pi N\mu}\right)^{1/2} \tag{11}$$

Thus the characteristic saturation radius r_{sat} is independent of the size of the ion and is determined only by its charge and the properties of the dielectric.[2] †

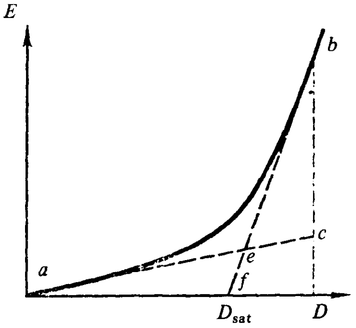

Figure 6. Dependence of the intensity of the electric field *E* on the electric induction *D*.

Comparison of the value of r_{sat} with the ionic radius a makes it possible to estimate how large a contribution the phenomenon of saturation may make to the energy of the electric field of the actual ion. For univalent ions in nitrobenzene with $N = 6 \times 10^{27}\ \text{m}^{-3}$ and $\mu_0 = 3.9$ D, it is found that $r_{\text{sat}} = 0.31$ nm, and in acetonitrile with $N = 1.1 \times 10^{28}\ \text{m}^{-3}$ and $\mu_0 = 3.97$ D, $r_{\text{sat}} = 0.29$ nm. For water ($N = 3.34 \times 10^{28}\ \text{m}^{-3}$, $\mu_0 = 1.84$ D), the characteristic saturation radius is 0.22 nm.

The values obtained are greater than the radii of monatomic inorganic ions, and for these the contribution of dielectric saturation to the energy of polarisation of the medium should be considerable. To find this contribution, it is necessary to calculate the density of the free energy of the electric field g, that is the integral (4). Approximating the latter by the area of the triangles *acd* and *fbd* in Fig.6 gives:

$$g = \frac{D^2}{2\varepsilon_0\varepsilon} \quad \text{for } D < D_{\text{sat}}$$

$$g = D^2/2\epsilon_0\epsilon + (D - D_{\text{sat}})^2/2\epsilon_0\epsilon_{\text{opt}} \text{ for } D > D_{\text{sat}}. \tag{12}$$

Integrating the density of the energy over the whole of space outside the ion gives the electric component of the solvation energy:

$$\Delta^{\alpha}_{\text{vac}}G^0(\text{el}) = -\frac{z^2e_0^2}{8\pi\varepsilon_0 a}\left[1 - \frac{1}{\varepsilon^{\alpha}} - \frac{1}{\epsilon^{\alpha}_{\text{opt}}}\left(1 - \frac{8}{3}x + 2x^2 - \frac{1}{3}x^4\right)\right] \tag{13}$$

where $x = a/r_{\text{sat}}$.

In addition to the Born term $1 - 1/\varepsilon^{\alpha}$, Eqn.(13) contains a correction to it which depends on the ratio of the radius of the ion a to the saturation radius. When $a = r_{\text{sat}}$, the correction becomes zero; it increases with decrease in a. This is understandable, since it is at short distances that dielectric saturation has an influence. For clarity, the equation obtained can be illustrated by numerical examples. Curve *2* in Fig.3 was constructed using Eqn.(13). It can be seen that allowance for saturation moves the Born straight line in the required direction, bringing it closer to the experimental points. The magnitude of the correction is different for different a. It is 16% for lithium ions. It was previously pointed out that for cations with a small radius, the deviation of the experimental points from the Born straight line reaches 30%. Thus in the case of lithium, allowance for saturation can eliminate more than half of the discrepancy. For potassium, the correction amounts to 4%, which covers 1/7 of the discrepancy between the theoretical and experimental values. Subsequently, the contribution from saturation decreases. It is 2.9% for rubidium, and 1.3% for caesium, corresponding to 0.1 and 0.04 times the required correction respectively.

Thus saturation of the dielectric constant has a significant influence on the electric component of the solvation energy only for the smallest ions, but in this case its influence may be extremely marked. Thus any continuum theory must take account of the saturation of the dielectric constant, at least in the calculation of the hydration energy of ions with a radius smaller than 0.15 nm.

The above estimate of the solvation energy with allowance for dielectric saturation was carried out within the framework of a rigorous continuum model. All the quantities were calculated from first principles. It was assumed that the dielectric constant changes regularly in space, without undergoing any sharp changes. For this reason, Eqn.(13) does not contain fitting parameters. In its derivation, no attempt was made to obtain a detailed description of the dependence of the electric induction on the intensity of the external electric field, and it was merely assumed that the true curve is fairly close to the two asymptotes (see Fig.6). For the complete curve, as already noted, there is a model description in the form of the Langevin function. It can be shown that in this approximation, the function *E(D)* rapidly reaches the second asymptote.

It should also be noted that the piecewise-linear approximation examined above leads to a slightly low value of E (for a given D), so that the values obtained for the solvation energy represent an upper estimate (absolute magnitude), although they are apparently close to the true value. The accuracy of the approximation increases with decrease in the radius of the ion. Detailed calculations based on the use of the Langevin function were carried out in Ref.53.

A simpler description of the phenomenon of saturation is given in Refs.47–52. To obtain simple analytical expressions, it is assumed that the dielectric constant changes in

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† See V.S.Markin and A.G.Volkov, J.Electroanal.Chem.(1987) (in the press).

stepwise fashion in space (see Fig. 4b). In this model it is assumed that the ion of radius a is surrounded by two solvate layers with radii b and c respectively. Within the first layer, complete dielectric saturation is assumed, and the dielectric constant is taken as equal to its optical value ($\varepsilon_1 = \varepsilon_{opt}$). At the boundary between the two layers, the dielectric constant undergoes an abrupt change, and in the second layer it has a new constant value ε_2, estimated from the Onsager–Booth equations.[42] Thus the electrostatic component of the solvation energy is given by the equation

$$\Delta^{\alpha}_{\rm vac}G^0({\rm el}) = -\frac{z^2e_0^2}{8\pi\varepsilon_0}\left[\left(1-\frac{1}{\varepsilon_1}\right)\left(\frac{1}{a}-\frac{1}{b}\right)+\right.$$
$$\left.+\left(1-\frac{1}{\varepsilon_2}\right)\left(\frac{1}{b}-\frac{1}{c}\right)+\left(1-\frac{1}{\varepsilon_2}\right)\frac{1}{c}\right] \qquad (14)$$

The use of the fitting parameters a, b, c, ε_1, and ε_2 gave almost complete agreement between the calculated and experimental data.[48] The value of $\Delta^{\alpha}_{\rm vac}G^0$(el) is practically insensitive to the parameter c; the use of the fitting parameter b gives the main contribution only if its value is so large as to be unreasonable. According to Ref. 48, to obtain the closest agreement between the theoretical and experimental results it must be assumed that for singly-charged inorganic ions within a radius of 0.4 nm round the ion there is complete dielectric saturation of the solvent, and $\varepsilon_1 = \varepsilon_{opt}$. From what has been said above, however, it is clear that this approach is unsound.

3. The Method of Non-local Electrostatics

To calculate the electrostatic contribution to the solvation energy, use is made of another semi-macroscopic approach, namely the method of non-local electrostatics, which has been developed extremely intensively in recent years. The method of non-local electrostatics takes account of the fact that the fluctuations of the polarisation of the solvent correlate with one another in space as a result of the presence in the liquid of a structure determined by the quantum-mechanical interaction between its molecules. Thus the average polarisation at each point depends on the induction at all other points in space, correlating with the given one.[54]

The relationship between the intensity of the electric field **E** and the electric induction **D** in the method of non-local electrostatics is expressed by means of the tensor $\varepsilon_{mn}(r)$:

$$D^m(\mathbf{r}) = \sum_n \int d\mathbf{r}\,\varepsilon_0\varepsilon_{mn}(\mathbf{r}-\mathbf{r}')E^n(\mathbf{r}') \qquad (15)$$

where $m, n = x, y, z$. A noteworthy feature is that this relationship, which has complex spatial character, remains linear. The subsequent calculations are carried out by the Fourier transformation of the tensor $\varepsilon_{mn}(\mathbf{r})$, which is called the static dielectric function $\varepsilon(\mathbf{k})$:

$$\varepsilon(k) = \sum_{m,n}\frac{k_mk_n}{k^2}\int {\rm d}(\mathbf{r}-\mathbf{r}')\,{\rm e}^{-ik(\mathbf{r}-\mathbf{r}')}\varepsilon_{mn}(\mathbf{r}-\mathbf{r}') \qquad (16)$$

The electric potential created in the medium by a charged sphere with a radius a at a distance r from its centre is

$$\varphi(\mathbf{r}) = \frac{ze_0}{2\pi^2\varepsilon_0}\int_0^{\infty}\frac{{\rm d}k}{\varepsilon(k)}\frac{\sin kr}{kr}\frac{\sin ka}{ka} \qquad (17)$$

This gives the electric contribution to the solvation energy:

$$\Delta^{\alpha}_{\rm vac}G^0({\rm el}) = -\frac{z^2e_0^2}{4\pi^2\varepsilon_0}\int_0^{\infty}{\rm d}k\,\frac{\sin^2 ka}{k^2a^2}\left[1-\frac{1}{\varepsilon(k)}\right] \qquad (18)$$

To calculate the integral in Eqn. (18), it is necessary to specify in some way the functional dependence $\varepsilon(k)$. It is possible, as was done in Refs. 33 and 34, to break down the fluctuations of the polarisation of the medium into three modes related to different degrees of freedom: electronic or optical (index 1), vibrational or infrared (index 2), and orientational or Debye (index 3). If the radius of the correlation of the i^{th} mode of a fluctuation is λ_i, then

$$1-\frac{1}{\varepsilon(k)} = 1-\frac{1}{\varepsilon_1}+\left(\frac{1}{\varepsilon_1}-\frac{1}{\varepsilon_2}\right)\frac{1}{1+k^2\lambda_2^2}+\left(\frac{1}{\varepsilon_2}-\frac{1}{\varepsilon_3}\right)\frac{1}{1+k^2\lambda_3^2} \qquad (19)$$

The correlation radius of the electronic mode λ_1 is here taken as zero. It is impossible to indicate beforehand the exact values of the correlation radii λ_2 and λ_3, but an approximate estimate can be carried out from physical considerations. For the infrared vibrations, the magnitude of λ_3 depends on the type of liquid. For non-associated liquids, the correlation radius of the orientational vibrations is approximately equal to the intermolecular distance, but for associated liquids, for example water, the scale of λ_3 is indicated by the characteristic length of the chain of hydrogen bonds, which amounts to ~0.5–0.7 nm.[33, 34]

Integration in Eqn. (18) using the function (19) gives the expression

$$\Delta^{\alpha}_{\rm vac}G^0({\rm el}) = -\frac{z^2e_0^2}{8\pi\varepsilon_0a}\left[1-\frac{1}{\varepsilon_1}+\left(\frac{1}{\varepsilon_1}-\frac{1}{\varepsilon_2}\right)\psi\left(\frac{2a}{\lambda^2}\right)+\left(\frac{1}{\varepsilon_2}-\frac{1}{\varepsilon_3}\right)\psi\left(\frac{2a}{\lambda_3}\right)\right] \qquad (20)$$

where

$$\psi(x) = 1-(1-e^{-x})/x \qquad (21)$$

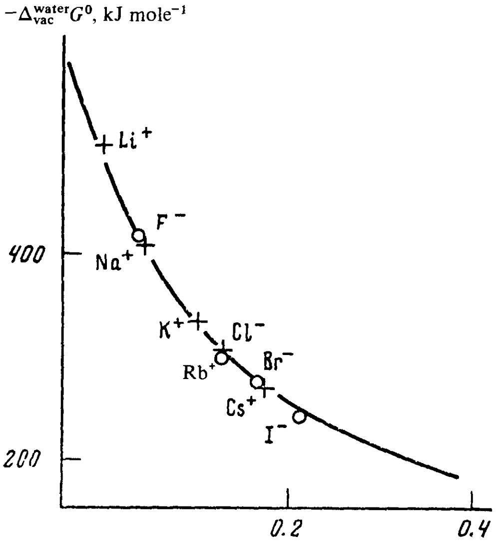

Figure 7. Dependence of the hydration energies of ions on their radius; the points give the experimental data,[29,30] and the continuous line the calculated data;[34] the values of a were taken from Ref. 31.

The electric contribution to the hydration energy, calculated[34] using these equations, is given in Fig. 7, together with the experimental data for a number of small univalent ions. The dielectric constant values used are given in Table 2. The correlation radii were chosen to be close to the characteristic values indicated from the condition for best agreement between the theoretical and experimental data: $\lambda_2 = 0.1$ nm and $\lambda_3 = 0.7$ nm. Fig.7 shows that good agreement was obtained between theory and experiment.[34] As far as the sensitivity of the results to the fitting parameters λ_i is concerned, λ_2 has the greatest weight, and a less significant role is played by λ_3, as shown in Fig.8. A detailed analysis was carried out in Ref.33. The method of non-local electrostatics essentially uses continuum models, but the effective parameters required for the calculation are derived from an analysis of the structure of the solvent. This method makes it possible to obtain extremely accurate values of the solvation energy for small ions, and then, using Eqn.(1), the values of the energy of resolvation. At the same time, for large ions, appreciable discrepancies are observed between theory and experiment. This indicates the need to take account of additional effects, in this case the work of formation of a cavity in the solvent, or the solvophobic effect.

Table 2. Values of the dielectric constants ε_i [28] used in the model of three polarisation modes (T = 293 K).

Solvent	$\epsilon_1 = \epsilon_{opt}$	ε_2	$\epsilon_3 = \epsilon_{st}$
Water	1.8	4.9	78.8
Nitrobenzene	2,4	3.7	35,0
1,2-Dichloroethane	2.0	—	10.4
Acetophenone	2,45	—	17.4
Dichloromethane	2,04	—	9.1
Methyl butyl ketone	1.9	—	14,9

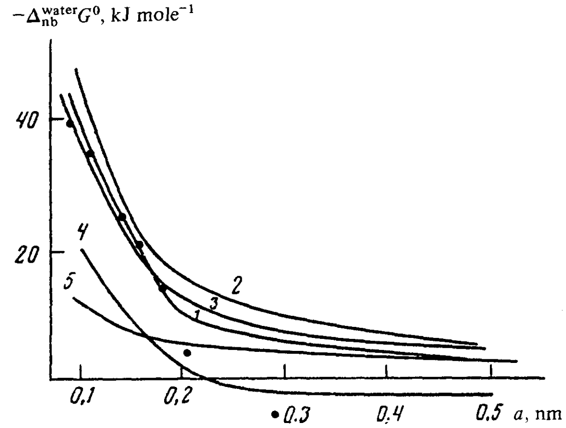

Figure 8. Influence of the spatial dispersion of the dielectric constants of the aqueous and nitrobenzene phases on the electrostatic contribution to the free energy of resolvation; the calculation was carried out by the published method[33] with $\lambda_2^{water} = 0.1$ nm and $\lambda_3^{water} = 0.7$ nm and the dielectric constants from Table 2; correlation radii, nm: *1)* $\lambda_2^{nb} = 0.1$, $\lambda_3^{nb} = 0.5$; *2)* $\lambda_2^{nb} = 0.1$, $\lambda_3^{nb} = 0.3$; *3)* $\lambda_2^{nb} = 0.13$, $\lambda_3^{nb} = 0.3$; *4)* $\lambda_2^{nb} = 0.1$, $\lambda_3^{nb} = 0.7$; *5)* calculated using the Born equation; the experimental data were taken from Table 1.

The chief disadvantage of the continuum and semi-continuum approaches to the problem of solvation lies in the actual model of the solvent. Allowance for saturation of the dielectric constant or correlation of the dipoles represents an attempt to reflect the discrete properties of the solvent while essentially remaining within the framework of the continuum model. Other similar approaches are known, in which, in the calculation of the thermodynamic properties of the system, attempts are made to take account of the unknown influence of the molecular structure of the solvent.[55] A true solution to the problem can be achieved, however, only by taking account of the discrete structure in the statistical theory of the solvent.

4. Statistical Models of the Solvent

A complete solution of the problem of solvation involves the development of a statistical theory which would regard the ions and solvent molecules "as equals", that is which would take account of their discrete molecular nature, even at the price of the introduction of model potentials.

In contrast to "primitive" models of an electrolyte, in which a continuum description of the solvent is used, in the "non-primitive" model used in present-day statistical analysis, or the ion–dipole plasma model, a solution of an electrolyte is regarded as a system of solid spheres with radii a and a_d, carrying at their centres a point electric charge or a constant point dipole respectively. It is assumed that there are the usual electrostatic interactions between the charges and the dipoles. The system is described in terms of many-particle correlation functions, for which corresponding chains of equations are written.[56–58] For their solution it is necessary to resort to various simplifications, among which the most popular is the mean-spherical approximation.[59] This model should make it possible to calculate the solvation energy of ions, and also the dielectric properties of a pure dipolar liquid.#

The dielectric constant of a dipolar liquid in the mean-spherical approximation was calculated in Ref.58, where the following equation was obtained:

$$\varepsilon = q(2\xi)/q(-\xi) \tag{22}$$

in which

$$q(x) = (1+2x)^2/(1-x)^4 \tag{23}$$

and the parameter ξ is obtained by solving the equation:

$$q(2\xi) - q(\xi) = n_d\mu^2/3\varepsilon_0 kT \tag{24}$$

Here, n_d is the number of particles of the solvent in unit volume, and μ the dipole moment of the solvent molecule. This approach made it possible to refine considerably the familiar Onsager equation.

For strongly associated liquids, the theoretical results do not show very good agreement with the experimental data. There is nothing surprising in this, since the model does not include a whole range of complex forces acting between real solvent molecules. For example, for a dipolar liquid having the same dipole moment of the molecules (1.8 D) as water, the dielectric constant obtained from Eqn.(22) at room temperature is 48. To obtain the correct value of $\varepsilon_{st} = 80$, it is necessary to take the value 2.62 D for the dipole moment of the molecules of the liquid.

A dipolar liquid is a model system consisting of solid spheres with dipoles situated at their centres. It is used in theoretical calculations of the properties of a liquid.

A model in the form of a set of solid spheres with constant dipole moments naturally cannot describe all the properties of water, but this system may serve as a reasonable model for organic solvents, and in any case this is the first necessary step in obtaining a model of water. In particular, the study of this model made it possible to detect a number of fundamentally important effects related to the solvation and interaction of ions and associated with the discrete nature of the solvent.

In Ref.59, the solvation energy of an ion (the "Born" energy) was calculated in the mean-spherical approximation:

$$\Delta^{\alpha}_{\mathrm{vac}} G^0 = -\frac{(ze_0)^2}{8\pi\varepsilon_0 (a + a_d/\lambda)}\left(1 - \frac{1}{\varepsilon}\right) \qquad (25)$$

where a_d is the diameter of the solvent molecule. The value of λ is determined by solving the equation

$$\lambda^2(1-\lambda)^4 = 16\,\varepsilon \qquad (26)$$

For all values of ε, the parameter λ lies in the range 1–3; for $\varepsilon = 80$ it is equal to 2.6. This parameter, together with the radius of the dipolar solvent molecule, defines in accordance with Eqn.(25) a new characteristic length a_d/λ, which arises naturally from the solution of the equations. This characteristic length is determined exclusively by the properties of the dipolar liquid, and depends on two of its parameters, the radius of the molecules and the dielectric constant.

Formally, Eqn.(25) looks like the equation for determining the Born energy, with a renormalised ionic radius, which has been increased by the section a_d/λ. An interesting feature is that there exists an empirical equation for describing the experimental solvation energies and free energies of resolvation, whose form is identical to that of Eqn.(25).[60] In aqueous electrolyte solutions, this correction lies in the range 0.64–0.84 Å for cations and 0.10–0.42 Å for anions. According to Eqn.(25), if the radius of the solvent molecule is taken as 1.5 Å, then $a_d/\lambda = 0.58$ Å.

The apparent increase in the radius of the ion in Eqn.(25) is related to the discrete nature of the solvent. It is obvious that the bulk value of the dielectric constant cannot be established directly at the actual "surface" of the ion. Eqn.(25) makes it possible to calculate that this value is effectively reached at a distance of $a + a_d/\lambda$ from the centre of the ion. It should be remembered, however, that this picture of a stepwise change in the dielectric constant represents only an effective approximation which can be used to describe a fairly accurate physical result obtained using the discrete model. Moreover, an analysis of this model shows that it is in general impossible to use the concept of local dielectric constant at such short distances, and it is necessary to return to the more accurate concept of the polarisation of the medium. In the macroscopic description of a dielectric, its polarisation at a distance r from the ion is given by the familiar equation $P_{\mathrm{macr}}(r) = (\varepsilon-1)ze_0/4\pi\varepsilon r^2$.

Fig.9a gives the calculated[59] dependence of the polarisation of the medium, normalised to its macroscopic value P_{macr}, on the distance r. The most important feature of this dependence is its oscillatory character. This means that, as a result of the strong ordering of the dipoles nearest to the ion, the subsequent dipoles may adopt the opposite orientation. For this reason, the description of a medium in terms of the local dielectric constant (for example, the use of the stepwise function), even if it gives good agreement with experiment, leads to erroneous ideas about the true physical picture at short distances, and this description must be approached with care.

An important consequence should be noted. The interaction of ions in a discrete medium differs fundamentally from that predicted by the macroscopic theory. This interaction is described by a potential of mean force W_{ij}, which, in addition to the Coulomb potential, includes the averaged interaction with all the solvent molecules. As shown by the same authors,[59] the potential of mean force also oscillates at short distances (Fig.9b). For example, the curve for ions of different kinds has a deep potential minimum W_{+-}, when the centres of the ions are at a distance of $4a$. This is a relatively stable configuration, in which the ions are separated by one dipolar molecule; it can be regarded as the result of the formation of ion pairs in the solution. The potential for ions of the same kind W_{++} also has a deep minimum, at $r = 3a$. This configuration gives as it were a "double" ion, for which the increase in the Coulombic energy is more than compensated by the negative displacement of the Born energy of solvation of the highly charged structure.

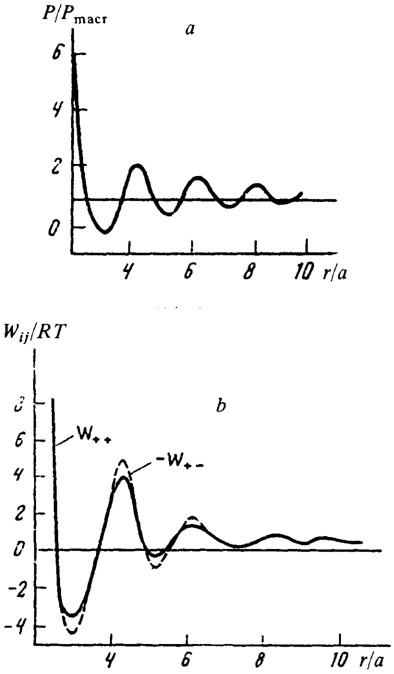

Figure 9. The normalised density of the polarisation P/P_{macr} (*a*) and the potential of the average force W_{ij} between two univalent ions i and j (*b*) as a function of the distance r from the centre of the ion.[59]

The results obtained in the mean-spherical approximation are mainly qualitative in character, but they make it possible to obtain a more correct representation of the true physical picture of solvation and to re-evaluate other theories on the basis of an understanding of how they achieve agreement with experiment.

III. THE SOLVOPHOBIC EFFECT

Present-day approaches to the calculation of the energy of the solvophobic interaction of an ion with a solvent are based on phenomenological[61,62] or statistical-mechanical molecular models,[63] which contain parameters, not always unknown, characterising the ion and the solvent. To avoid unnecessary indeterminacy, the estimation of the solvophobic contribution to the free energy of resolvation is sometimes carried out using Uhlig's semi-empirical equation,[64] the essential features of which reduce to the following.

If the concept of the surface tension at the boundary of the ion and the solvent $\gamma_{0,\alpha}$ is used, the surface energy is $4\pi a_2\gamma_{0,\alpha}$. The difference in the surface energies in the media α and β is $4\pi a^2(\gamma_{0,\alpha}-\gamma_{0,\beta})$. According to Antonov's rule

$$\gamma_{0,\alpha}-\gamma_{0,\beta}\approx\gamma_{\alpha\beta}\,\mathrm{sgn}\,(\gamma_\alpha-\gamma_\beta) \qquad (27)$$

where sgn $x = +1$ if $x \geq 0$, and sgn $x = -1$ if $x < 0$, $\gamma_{\alpha\beta}$ is the interfacial tension at the planar boundary between the media α and β, and γ_α and γ_β the surface tensions at the boundaries between air and the solvents α and β respectively at the same pressure and temperature. In this case, Uhlig's equation for the solvophobic contribution to the energy of resolvation has the form:

$$\Delta_\beta^\alpha G^0(\mathrm{svph}) = 4\pi a^2\gamma_{\alpha\beta}\,\mathrm{sgn}\,(\gamma_\alpha-\gamma_\beta) \qquad (28)$$

The contribution is obviously greater, the larger the radius of the ion *a*.

From the theoretical viewpoint, the range of applicability of Uhlig's equation is not quite clear. At the same time, it has proved surprisingly useful in calculations of distribution coefficients in systems consisting of two immiscible liquids.[33,34] Slight deviations from Uhlig's equation are observed when the interfacial tension between the two pure immiscible solvents is less than 10 mN m^{-1} and the dissolved species have dimensions of less than 0.2 nm.[35] This can readily be explained, since Uhlig's equation neglects the dependence of the surface tension on the curvature of the surface. At low values of $\gamma_{\alpha\beta}$ and for small particles, the contribution of the solvophobic effect is slight.

An important advantage of Uhlig's equation is that it does not contain fitting parameters, since $\gamma_{\alpha\beta}$ is taken from experiment. Fig.10 gives as an example the dependence of the solvophobic contribution to the energy of resolvation on the radius of the particle, calculated from Eqn.(28), for the water-nitrobenzene and water–1,2-dichloroethane systems.

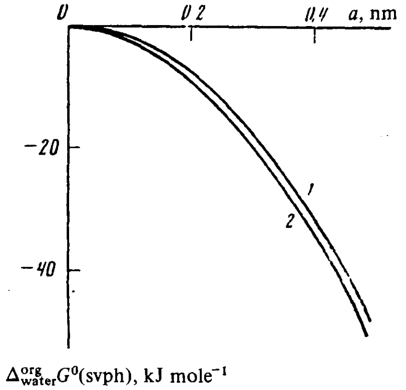

Figure 10. Solvophobic contribution to the energy of resolvation of a particle of radius *a* from water into nitrobenzene (*1*) and 1,2-dichloroethane (*2*), calculated using Uhlig's equation.[34]

IV. THE TOTAL ENERGY OF RESOLVATION

Various effects making a contribution to the energy of resolvation of ions were listed above. For most solvents of interest, the most significant role is played by electrostatic and solvophobic effects.[33] This has made it possible to represent the energy of resolvation as the sum of the contributions of two effects:[33]

$$\Delta_\beta^\alpha G^0 = \Delta_\beta^\alpha G^0(\mathrm{el}) + \Delta_\beta^\alpha G^0(\mathrm{svph}). \qquad (29)$$

The non-electrostatic part of the energy is usually taken as equal to the energy of solvation of the hypothetical discharged ion, all of whose other characteristics remain unchanged. It is usually estimated by comparing with a suitable neutral analogue, for example a noble gas. It is assumed that the energies of the formation of the cavity and the change in the structure of the solvent are the same for particles with the same shape and size, irrespective of the charge. This approach has an important advantage, emphasized in Ref.48. If identical standard states in the gas phase and the solution are taken for the ion and the neutral species imitating it, this procedure removes completely the problem of the recalculation and loss of the translational entropy of the solute in the solution in the comparison of the theoretical results with the experimental data.

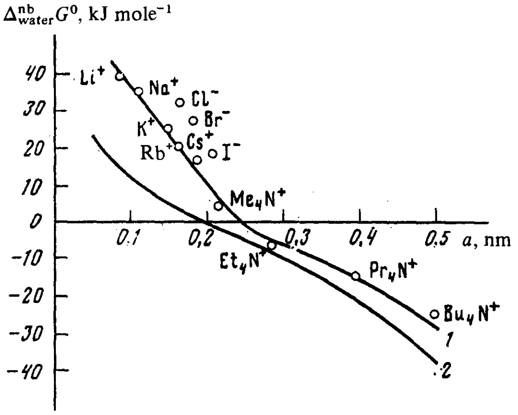

Figure 11. Dependence of the energy of resolvation on the radius of the ion in the water–nitrobenzene system, calculated from Eqn.(29): *1*) using the method of non-local electrostatics;[33,34] *2*) using the Born equation; the points give the experimental data (see Table 1).

In Ref.33, the electrostatic contribution was calculated by the method of non-local electrostatics, and the solvophobic contribution using Uhlig's equation. The results of the calculation for the most extensively studied experimental water–nitrobenzene system are given in Fig.11 (curve *1*). Comparison with curve *2*, obtained by calculation using

Born's equation, shows that allowance for the solvophobic effect alone does not make it possible to compensate the inadequacies of this simple equation.

Fig.11 shows that as a result of the solvophobic effect, the energy of resolvation may change sign with change in the radius of the ions. The results of the calculation show very good agreement with the experimental data. The deviations observed for anions in the range of small radii may be due to the formation of hydrogen bonds between the anions and the solvent molecules, or to the phenomenon of defect annihilation. The magnitude of these deviations corresponds approximately to the energy gain resulting from the formation of a weak hydrogen bond between the anion and the solvent.

The values of the energy of resolvation of small anions obtained by different authors differ considerably from one another.

V. STANDARD DISTRIBUTION POTENTIALS

When the energy of resolvation of an ion is known, it is possible to calculate the standard distribution potential $\Delta_\beta^\alpha\phi_i^0$ from the equation

$$\Delta_\beta^\alpha\varphi_i^0=-\frac{\Delta_\beta^\alpha G_i^0}{z_i F} \qquad (30)$$

where F is the Faraday constant.

Table 1 gives the distribution potentials for different ions between water and organic solvents. In the separation of the standard free energy of resolvation into ionic components and the determination of the distribution potentials, the tetraphenylborate hypothesis was used.[65–69]

It is known from thermodynamics that the absolute value of a difference in electric potentials can be measured only in conductors with the same composition. For the same reason, the difference in the galvanic potentials between a point in an aqueous phase and a point in the depth of an organic solvent cannot be measured experimentally.

If identical reversible electrodes are introduced into each of the phases of two immiscible electrolyte solutions in thermodynamic equilibrium, the inter-phase potential difference between them will be zero, since the system, being in equilibrium, cannot perform work.[70] If the reversible electrodes are different, the measured potential difference will be equal to that which would have been observed if these electrodes had been placed in the same solution.[70]

The following experimental methods are now used to measure distribution potentials and also to determine $\Delta_\beta^\alpha G^0$: polarography at a dropping electrolyte electrode;[1,12,15,27,71,72] polarography with scanning of the current at a dropping electrolyte electrode;[73–75] polarography at a rising aqueous electrode;[76] alternating-current polarography;[77–80] chronopotentiometry;[80–82] chronoammetry;[80,83] cyclic voltammetry;[12,18,22,71,84–88] measurement of the EMF of liquid circuits;[25,89,90] calculation using data on solubility,[14] distribution coefficients,[24,91–95] extraction,[91,96,97] the spin-lattice relaxation of the quadrupolar nuclei of the ions,[23,98,99] and calorimetry.[100] The accuracy of the measurement of $\Delta_\beta^\alpha\phi^0$ and $\Delta_\beta^\alpha G^0$ reaches 1 mV and 0.1 kJ mole^{-1} respectively.

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The present review has described the most effective present-day methods for calculating the free energy of resolvation of ions. The most successful approach involves the use of the electrostatics of the media with spatial dispersion with allowance for solvophobic effects.

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Methods of Synthesis of Compounds with Halogenoimidoyl Groups

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The available information about the methods of synthesis of compounds of different classes containing the halogeno-imidoyl group $-\mathrm{N}=\overset{|}{\mathrm{C}}-\mathrm{Hal}$ are surveyed and the application of the known methods of synthesis of such compounds to new objects is examined. Data are presented on new methods of synthesis of compounds containing the $-\mathrm{N}=\overset{|}{\mathrm{C}}-\mathrm{Hal}$ group which have been developed in recent years.

The bibliography includes 239 references.

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I. INTRODUCTION

Compounds containing the halogenoimidoyl group $-\mathrm{N}=\mathrm{C}-\mathrm{Hal}$ are extremely varied and have continually attracted the interest of investigators as a consequence of the high reactivity of the group, which makes it possible to involve them in a large number of reactions with formation of various acyclic and heterocyclic substances.[1-3] Furthermore, the interest in such compounds is due to the broad spectrum of the physiological activity of either the compounds themselves or the products of their reactions.[4-7]

Monographs and reviews devoted to the methods of synthesis and reactions of compounds of this large class are now available but they were published more than 15 years ago.[1,2] Thorough reviews covering the work of recent years are concerned mainly with imidoyl fluoride and fluorinated imidoyl halides,[8-11] hydrazonohalides [halogenocarbonyl hydrazones (Ed.of Translation)], and halogenoazines.[12-14] Fragmentary data on compounds with halogenoimidoyl groups have been included in several monographs.[15-22]

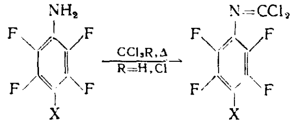
The aim of the present review is to survey data on the methods of synthesis of compounds containing the $-\mathrm{N}=\overset{|}{\mathrm{C}}-\mathrm{Hal}$ group published between 1970 and 1986. It includes as a rule recent studies which have not been covered by the existing reviews. For this reason, few data are presented on imidoyl fluoride and difluorides and also on *N*-halogeno-compounds. In the case of hydrazonohalides and halogenoazines, attention has been concentrated on studies published after 1974 and 1977 respectively. With the exception of a few examples, the review does not deal with heterocyclic compounds in which the halogenoimidoyl group forms part of the heterocycle or is attached to it.

Analysis of the literature data on the synthesis of various compounds with halogenoimidoyl groups up to 1970 permits the conclusion that, together with the development of the traditional methods of synthesis of such compounds, fundamentally new methods of their synthesis have been developed in the last 15 years and have expanded the range of these compounds and their possible applications.

II. SYNTHESES FROM AMINES, *N*-HALOGENOAMINES, AND HYDRAZINES

1. Thermolytic and Photochemical Reactions of Amines and *N*-Halogenoamines

A novel thermolytic method of synthesis of polyfluorinated *N*-(aryl)-carboimidoyl dichlorides not described previously, has been proposed comparatively recently. It consists in the copyrolysis of polyfluorinated primary aromatic amines with $CHCl_3$ or CCl_4 in a flow system at 600–670 °C:[23,24]



X = H, Cl, Br, F, CF_3, CN

The reaction is fairly general for polyfluorinated benzene derivatives and has been extended also to 2-aminoheptafluoronaphthalene and 4-amino-2,3,5,6-tetrafluoropyridine. The yield of carboimidoyl dichloride is 14–34%. The copyrolysis with CCl_4 takes place at a lower temperature, with a smaller excess of the halogenomethane and with a higher yield than the reaction with $CHCl_3$. The polyfluorinated *N*-(aryl)carboimidoyl dichlorides are also formed on copyrolysis of *N*-chloroamines with $CHCl_3$.

The disadvantages of the method include the low yield of the carboimidoyl dichloride, the high content of the polychlorinated products of the thermolysis of $CHCl_3$ and CCl_4 in the reaction mixture, and in certain cases side reactions of the substituents in the initial amine.

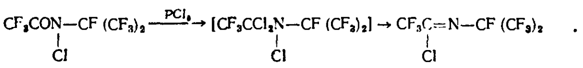
The formation of carboimidoyl dichlorides from amines and $CHCl_3$ apparently includes the preliminary generation of dichlorocarbene. However, the available data do not formally conflict with the participation in the reactions with $CHCl_3$ also of the trichloromethyl radical. The latter process is apparently the main one in the copyrolysis of amines with CCl_4.

The method of synthesis of carboimidoyl dichlorides indicated above has no analogies in the series of non-fluorinated compounds. The attempts to extend it to non-fluorinated amines, for example, aniline, was unsuccessful. The reason may be the thermal instability of the initial amines at high temperatures.

The copyrolysis of aromatic polyfluoroamines with pentafluorotrichloromethylbenzene at 500–520 °C leads to *N*-(polyfluoroaryl)pentafluorobenzimidoyl chlorides.[25] The yield is 50–77% in most cases. It has been suggested that the reaction proceeds via a radical pathway, although the possibility of the nucleophilic substitution of chlorine in pentachlorotrichloromethylbenzene under severe copyrolysis conditions is not ruled out.

The formation via a radical pathway of *N*-(pentafluorophenyl)carboimidoyl fluoride chloride as one of the products has been noted[26] in the pyrolysis of *N*-4-dichloroperfluorocyclohexa-2,5-dienylideneamine (550 °C, 1 mmHg) in a flow system.

Unstable *N*-chloroamines also having a chlorine atom at the α-carbon atom are very readily dechlorinated and are converted into the corresponding imidoyl chlorides even at room temperature:[27]



$$CF_3CON(Cl)\text{—}CF(CF_3)_2 \xrightarrow{PCl_5} [CF_3CCl_2N(Cl)\text{—}CF(CF_3)_2] \rightarrow CF_3C(Cl){=}N\text{—}CF(CF_3)_2 \quad .$$

In the photolysis of a mixture of t-butylamine with trifluoromethylbenzenes, *N*-(t-butyl)benzimidoyl fluorides are formed as the main products, but their yields are low and the process cannot be regarded as preparative.[28]

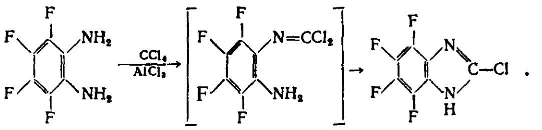
2. Reactions of Amines, *N*-Chloroamines, and Hydrazines in the Presence of Lewis Acids

A new method of synthesis of carboimidoyl dichlorides and chlorides involves the reaction of weakly basic amines with compounds of the type CCl_3R in the presence of $AlCl_3$. Thus heating of aromatic polyfluoroamines with CCl_4 and $AlCl_3$ at 40–80 °C leads to *N*-(polyfluoroaryl)carboimidoyl dichlorides in yields of 40–90%:[29,30]

$$Ar_FNH_2 \xrightarrow[AlCl_3]{CCl_4} Ar_FN{=}CCl_2$$

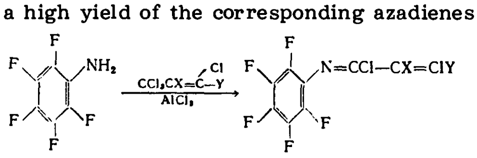
The reaction is fairly general for polyfluorinated benzene, biphenyl, naphthalene, and heterocyclic amine derivatives. The corresponding carboimidoyl dichlorides have been obtained in this way from pentafluoroaniline and *p*-substituted tetrafluoroanilines (the *p*-Br, *p*-Cl, *p*-NO_2, *p*-CN, and *p*-CH_3 derivatives and also the compound with H in the *p*-position), as well as pentachloroaniline. Compared with the pyrolytic method,[23,24] this procedure gives an increased yield and a greater range of products.

Tetrafluoro-*m*-phenylenediamines and tetrafluoro-*p*-phenylenediamines also enter into this reaction, which takes place in steps and leads to a mixture of mono- and di-carboimidoyl dichlorides with the latter predominating. On the other hand, the interaction of tetrafluoro-*o*-phenylenediamine with CCl_4 and $AlCl_3$ takes place in a more complex manner and leads to 2-chloro-4,5,6,7-tetrafluorobenzimidazole. It may be that the reaction proceeds via the intermediate *N*-(2-amino-3,4,5,6-tetrafluorophenyl)carboimidoyl dichloride, like the formation of benzimidoyl derivatives from the intermediate *o*-aminoarylamidoyl fluorides:[31]



The reaction with 4-amino-2,3,5,6-tetrachloropyridine takes place fairly smoothly.[32] In contrast to this, 4-amino-2,3,5,6-tetrafluoropyridine does not react.[30] Non-fluorinated amines react with CCl_4 and $AlCl_3$ to form carboimidoyl dichloride only if their basicity is sufficiently low. Thus *p*-nitroaniline is converted into *N*-(*p*-nitrophenyl)carboimidoyl dichloride, while aniline forms a high-melting salt-like product.[30]

Aluminium chloride is a specific catalyst in the process. Other Lewis acids proved to be virtually ineffective.[30] The replacement of CCl_4 by trichloromethylbenzene and its derivatives leads to the formation of the corresponding imidoyl chlorides even at room temperature.[30,33] Polyhalogenopropenes containing the CCl_3 group at the C=C aliphatic bond also react very readily with pentafluoroaniline, affording a high yield of the corresponding azadienes:[34]



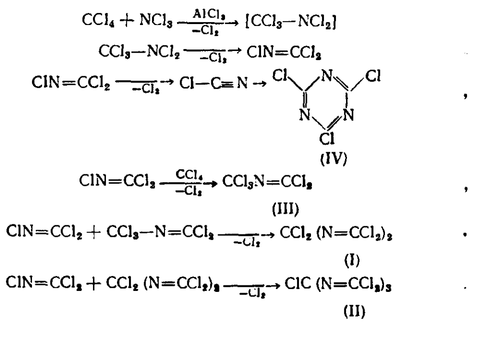
X = F, Y = Cl; X = Y = Cl; X = F, Y = C_6F_5

Hexafluorobenzene, $CHCl_3$, and CH_2Cl_2 are inert solvents for these reactions. In the synthesis of carboimidoyl dichloride and chloride by the above method, account must be taken of the side processes due to the effect of $AlCl_3$, for example, the exchange of fluorine for chlorine in the fluoroalkyl groups.[30]

One of the possible mechanisms of the formation of imidoyl chlorides and dichlorides from aromatic amines and compounds with the trichloromethyl group in the presence of $AlCl_3$ involves the formation of complexes by $AlCl_3$ with the trichloromethyl derivatives and the amine and subsequent conversion of the amine into the chloroalkyl derivative and further into the final product:[30]

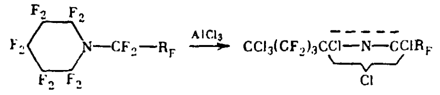
$$ArNH_2 + [R\overset{\delta+}{C}Cl_2 \ldots Cl \ldots \overset{\delta-}{Al}Cl_3] \rightarrow [Ar\overset{+}{N}H_2\text{—}CCl_2R] \xrightarrow[-H^+]{} [ArNHCCl_2R] \rightarrow$$
$$\xrightarrow[-HCl]{} ArN{=}CClR$$

The reaction of nitrogen trichloride with CCl_4 in the presence of $AlCl_3$ also leads to carboimidoyl chlorides,[35,36] but in this case a mixture of compounds is formed, whose proportions can be changed by varying the reaction conditions. It is of interest that bis- and tris-(carboimidoyl dichlorides) (I) and (II) have been obtained in this way. Small amounts of compound (III) and cyanuric chloride (IV) were isolated from the reaction mixture together with the above compound. The following mechanism of the reactions has been proposed:



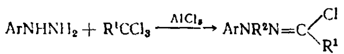
$$CCl_4 + NCl_3 \xrightarrow[-Cl_2]{AlCl_3} [CCl_3\text{—}NCl_2]$$
$$CCl_3\text{—}NCl_2 \xrightarrow[-Cl_2]{} ClN{=}CCl_2$$
$$ClN{=}CCl_2 \xrightarrow[-Cl_2]{} Cl\text{—}C{\equiv}N \rightarrow \text{(IV)} \quad ,$$
$$ClN{=}CCl_2 \xrightarrow[-Cl_2]{CCl_4} \underset{\text{(III)}}{CCl_3N{=}CCl_2} \quad ,$$
$$ClN{=}CCl_2 + CCl_3\text{—}N{=}CCl_2 \xrightarrow[-Cl_2]{} \underset{\text{(I)}}{CCl_2(N{=}CCl_2)_2} \quad .$$
$$ClN{=}CCl_2 + CCl_2(N{=}CCl_2)_2 \xrightarrow[-Cl_2]{} \underset{\text{(II)}}{ClC(N{=}CCl_2)_3} \quad .$$

On treatment of perfluorinated cyclic tertiary amines with CCl_4 and $AlCl_3$, imidoyl chlorides with a linear structure are formed.[37,38] In this case, the mobile fluorine atoms in the α-position with respect to the nitrogen atom in the complex of the amine and $AlCl_3$ are exchanged for chlorine under the influence of the excess $AlCl_3$ with subsequent rearrangement of the αα'α''-polychloroamines, which are unstable under these conditions, to the sterically less hindered imidoyl chlorides. The rearrangement is accompanied by the dissociation of the C–N bond in the ring:



$R_F = (CF_3)_2CF—, CF_3CF_2CF_2—$.

The weakly basic hydrazines (V) also react with compounds having trichloromethyl groups and $AlCl_3$.[39] Pentafluorophenylhydrazine and *p*-nitrophenylhydrazine react with CCl_4 or trichloromethylbenzene and $AlCl_3$ and are converted into the corresponding *N*-(aryl)hydrazonodichloromethanes or *N*-(aryl)phenylhydrazonochlorides:



$$\underset{(V)}{ArNHNH_2} + R^1CCl_3 \xrightarrow{AlCl_3} ArNR^2N{=}C\begin{matrix}\diagup Cl\\ \diagdown R^1\end{matrix}$$

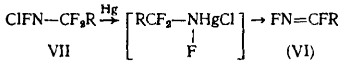
$Ar = C_6F_5$	$R^1 = Cl$	$R^2 = CCl_3$
C_6F_5	C_6F_5	H
C_6F_5	C_6H_5	H
$4NO_2-C_6H_4$	Cl	H

The direct conversion of arylhydrazine into arylhydrazonochlorides had not been noted earlier in the literature.

N-(Trifluoromethyl)carboimidoyl dibromide was obtained in 93% yield by the reaction of bis(trifluoromethyl)amine with CF_2Cl_2 and BBr_3.[40]

3. Other Reactions of Amines with *N*-Halogenoamines

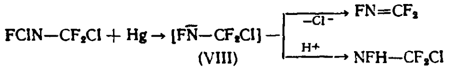
A method has been proposed for the synthesis of *N*-fluoroimidoyl fluorides (VI) in a satisfactory yield by dehalogenating amines of the type $NFClCF_2R$ (VII) by heating with mercury in the absence of a solvent.[41,42] The reaction mechanism has not been established accurately, but it has been suggested that it involves the insertion of mercury in the N–Cl bond and subsequent formation of the intermediate mercury compound:



$$\underset{VII}{ClFN—CF_2R} \xrightarrow{Hg} \left[\begin{matrix}RCF_2—NHgCl\\ |\\ F\end{matrix}\right] \rightarrow \underset{(VI)}{FN{=}CFR} \quad ;$$

$R = CF_3, C_2F_5, CF_2NClF$.

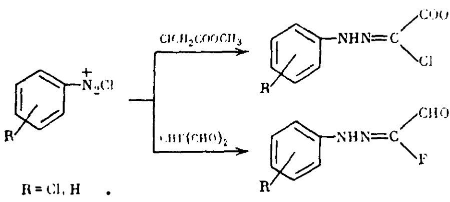
N-Fluorocarboimidoyl difluoride (VI, R = F) is formed in this way from the amine (VII, R = F) in yields up to 60%, but it cannot be separated from the impurities produced. A product which was readily purified was obtained in 90% yield by carrying out the reaction in trifluoroacetic anhydride. The use of trifluoroacetic acid as the solvent at 0 °C led to a mixture of the difluoride (VI, R = F) and *N*-(chlorodifluoromethyl)-*N*-fluoramine. Apparently the intermediate anion (VIII) is formed in the reaction in solvents and readily loses Cl^-, affording imidoyl difluoride, or abstracts a proton from the solvent and is converted into an amine:



$$FClN—CF_2Cl + Hg \rightarrow \underset{(VIII)}{[F\bar{N}—CF_2Cl]} — \begin{cases} \xrightarrow{-Cl^-} FN{=}CF_2 \\ \xrightarrow{H^+} NFH—CF_2Cl \end{cases} ,$$

Other amines of the type R_FNClF are converted only into *N*-(fluoroalkyl)-*N*-fluoramines under these conditions. *N*-(Chloro)trifluoroacetimidoyl fluoride has been obtained in a moderate yield from *NN*-dichloro-*N*-(perfluoroethyl)-amine on interaction with mercury in trifluoroacetic acid.

The coupling of diazotised anilines with methyl α-chloroacetate or fluoromalonaldehyde leads respectively to *N*-(aryl)-hydrazonochlorides or fluorides:[43-45]

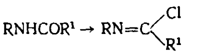


III. SYNTHESES FROM COMPOUNDS WITH THE –NHCO OR –NHCS GROUP

The conversion of the –NHCO or –NHCS group into $-N{=}\overset{|}{C}-Hal$ on treatment with various halogen-containing reagents is the basis of well known and widely used methods of synthesis of halogenoimidoyl derivatives. Most of the studies in recent years on these lines have been associated with the involvement of new compounds in the reaction already described previously.

1. Reactions with Halogeno-derivatives of Phosphorus and Sulphur and with Halogens

One of the simplest and most convenient methods of synthesis of imidoyl halides is the halogenation of amides by phosphorus halides or $SOCl_2$. The following reactions have been carried out using PCl_5 and $SOCl_2$:



$$RNHCOR^1 \rightarrow RN{=}C\begin{matrix}\diagup Cl\\ \diagdown R^1\end{matrix} \quad \cdot$$

$R = CH_3$	$R^1 = C_6H_5, 4\text{-}XC_6H_4, COOC_2H_5$ (Refs.46-48)
$OCOCF_3$	CF_3 (Ref.49)
$CCl_3CHOH, CHClBrCHCl$	$C_6H_5, 4\text{-}XC_6H_4, CH_3$ (Refs.50-52)
$CCl_3CHCl, CCl_2 = CH$	$CHCl_2, CCl_3, C(CH_3)_3$
SF_5	CF_3, CH_3 (Ref.53)
$OCH_3, OC_2H_5, OC_3H_7\text{-m}$	$C_6H_5, 4\text{-}XC_6H_4$ (Refs.54-57)
$OC_3H_7\text{-iso}, OC_4H_9\text{-n}$	$2,4\text{-}XYC_6H_3$
$4\text{-}XC_6H_4CH_2, C_6H_5CH_2$	$C_6H_5, 4\text{-}NO_2C_6H_4$ (Ref.58)
$C_6H_5, 4\text{-}XC_6H_4$	$2CF_3SO_2C_6H_4, C_6H_5, 4\text{-}XC_6H_4$ (Refs.59-60).

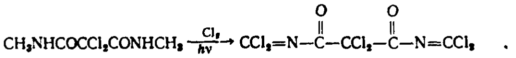
The corresponding imidoyl bromide has been obtained from compound (IX, $R = OCH_3$, $R^1 = C_6H_5$) by reaction with PBr_3, but its yield was low;[56] an alternative method of synthesis with a yield of 51% involves the nitrosative deamination of *o*-methylbenzamide oxime in HBr.[57] *N*-Phenylbenzimidoyl bromide can be obtained from benzanilide and PBr_5 only in a mixture with the product of the bromination in the *p*-position of the aromatic ring attached to the nitrogen atom.[61]

It is of interest to note that the trichloroacetyl derivative of pentachloroaniline is converted into *N*-(pentachlorophenyl)trichloroacetimidoyl chloride on reaction with PCl_5,[62] while *N*-(pentafluorophenyl)trichloro- or -trifluoro-acetimidoyl chloride cannot be obtained from the corresponding anilides and PCl_5. Under the reaction conditions, they are converted into trichlorophosphazopentafluorophenyl.[63] The formation of organophosphorus compounds instead of the expected hydrazonochlorides has been observed also in the interaction of *N*-phenyl- and *N*-methyl-*N*-trifluoroacetohydrazides with PCl_5.[64]

In the case of the *o*-azidobenzanilides or *N*-(*o*-azidobenzoyl)anilides, the imidoyl chlorides formed rapidly cyclise to derivatives of 2*H*-indazole or benzimidazole, so that they cannot be isolated, although there is no doubt about their intermediate formation.[65,66]

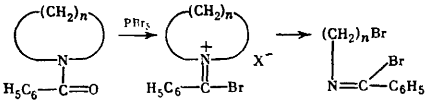
An *o*-allyl-substituted imidoyl chloride has been obtained from the *o*-allylbenzoyl derivative of *p*-nitrobenzylamine.[67] Various 2-phenylethylamides react with reagents of the type of PCl_5, $POCl_3$, and $SOCl_2$ under mild conditions to form imidoyl halides in high yields.[68,69] This finding proved to be extremely important for the understanding of the mechanism of the formation of derivatives of dihydroisoquinoline from amides and $POCl_3$ in the classical Bischler–Napieralski reaction. It permitted the conclusion that imidoyl chlorides are formed as intermediates in this reaction and made it possible to modify the conditions for its occurrence in order to attain the highest yield of the cyclisation product.

The chlorination of *NN'*-dichlorodimethylmalonamide with chlorine under UV irradiation proceeds differently to the reactions of amides described above, although it also leads to a compound with imidoyl dichloride groups:[70]



$$CH_3NHCOCCl_2CONHCH_3 \xrightarrow[h\nu]{Cl_2} CCl_2{=}N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CCl_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N{=}CCl_2 \quad .$$

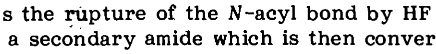
Amide groups forming part of the heterocyclic ring are converted into imidoyl chlorides on treatment with PCl_5 or $POCl_3$. Chlorine-containing quinazolines,[71] phthalazines,[72] 1,2,4-triazines,[73] pyrazines,[74] pyridazines,[75,76] isoindolenines,[77] and phenanthridines[78,79] have been synthesised in this way. Cyclic benzamides of type (X) react with PBr_5 with ring opening and the formation of *N*-(ω-bromoalkyl)imidoyl bromides (XI). The reaction proceeds via the intermediate iminium bromide (XII):[80]



(X) (XII) $X = Br_3^-; Br^-$. (XI) .

A mixture of $SOCl_2$ and SO_2Cl_2 is as a rule used for the synthesis of carboimidoyl dichloride from amides. The corresponding *N*-arylcarboimidoyl dichlorides have been obtained in this way from formanilide and its 2,6-dichloro- and 2,4,5-trichloro-derivatives.[81] However, the attempt to use this method to synthesise *N*-pentafluorophenylcarboimidoyl dichloride was not very successful.[82]

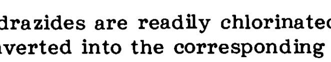
The synthesis of *N*-pentafluorophenyl)perfluoropropylimidoyl fluoride by treating a tertiary amide with SF_4 in HF has been described:[83]



$$C_6F_5N(COC_3F_7)_2 + SF_4 \xrightarrow{HF} C_6F_5N{=}C\begin{matrix}\diagup F \\ \diagdown C_3F_7\end{matrix} \quad .$$

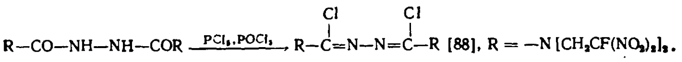
The yield of the product is 73%. The proposed reaction pathway involves the rupture of the *N*-acyl bond by HF and the formation of a secondary amide which is then converted into the imidoyl fluoride. Thiobenzanilide reacts with SF_4 and is converted into *N*-phenylbenzimidoyl fluoride in 52% yield.[84]

Like amides, hydrazides are readily chlorinated by $SOCl_2$ or PCl_5, being converted into the corresponding hydrazonochlorides:



$$R^1CONHNR^2R^3 \rightarrow R^1{-}\underset{\underset{\displaystyle Cl}{|}}{C}{=}N{-}NR^2R^3$$

$R^1 = 2\text{-}BrC_6H_4, 2\text{-}FC_6H_4$; $R^2 = H$; $R^3 = C_6H_5$ (Ref.85); $R^1 = C_6H_5$, $R^2 = H$, $R^3 = C_6F_5$ (Ref.86); $R^1 = R^3 = C_6F_5$; $R^2 = H$; $R^1 = t\text{-}C_4H_9, C_6H_5$; $R^2 = CH_3$; $R^3 = 2,4\text{-}(NO_2)_2C_6H_3, 4\text{-}NO_2C_6H_4, C_6H_5$ (Ref.87); $R^1 = C_6H_5$; $R^2 = H$; $R^3 = Ts$ (Ref.13);

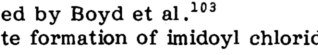


$$R{-}CO{-}NH{-}NH{-}COR \xrightarrow{PCl_5, POCl_3} R{-}\overset{\overset{\displaystyle Cl}{|}}{C}{=}N{-}N{=}\overset{\overset{\displaystyle Cl}{|}}{C}{-}R \text{ [88]}, R = {-}N[CH_2CF(NO_2)_2]_2 .$$

A convenient modification of the method involves treating the hydrazides with the $POCl_3$.pyridine complex in an excess of $POCl_3$.[12,89–91] On treatment with PCl_5, certain hydrazides undergo a rearrangement in the course of which the intermediate formation of compounds with the imidoyl chloride functional groups is postulated.[92]

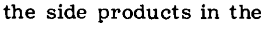
On treatment with PCl_5, arylureas are converted in high yields into *N*-arylbenzimidoyl chlorides,[93] while *N*-alkylideneureas are converted into chloro-1,3-diaza-1,3-dienes.[94] Compounds of a similar type with two conjugated imidoyl chloride groups are obtained by chlorinating *N*-thioaroyl-*N'*-arylthioureas.[95]

Chlorination of perfluoroalkylthioanilides leads to *N*-phenylimidoyl chlorides in high yields:[84]



$$C_6H_5NHCSCF_3 \xrightarrow{Cl_2} C_6H_5N{=}C\begin{matrix}\diagup Cl \\ \diagdown CF_3\end{matrix}$$

The formation of a small amount (up to 10%) of relatively unstable *N*-pentafluorothioimidoyl chlorides, characterised spectroscopically, has been noted in the reactions of *N*-pentafluorothiourethanes or thiourethanes with PCl_5:[96]



$$SF_5NHCOR \rightarrow SF_5N{=}C\begin{matrix}\diagup Cl \\ \diagdown R\end{matrix} \quad ,$$

$R = OC_6H_5, SCH_3, SC_6H_5$.

2. Reactions with the Vilsmeier Reagent and Its Analogues

The reactions of amides with the Vilsmeier reagent proceed in a more complex manner. Thus, when acetanilides interact with this reagent, imidoyl chlorides are formed only as intermediates, which are subsequently converted into formamidines, 2-chloroquinolines, or other heterocyclic derivatives depending on the substituent in the acetanilide and the reaction conditions.[97–101] The interaction of the Vilsmeier reagent with 2- and 3-acetamidothiophens proceeds analogously.[98,102] The reaction of the Vilsmeier reagent with *NN*-dimethylurea has been described by Boyd et al.[103]

The intermediate formation of imidoyl chlorides has been postulated in the reactions of anilides of the type $ArNHCOCH_2R$ with the aza-analogues of the Vilsmeier reagent obtained from $POCl_3$ and *N*-nitrosodimethylamine or its homologues.[100] However, *N*-(*m*-tolyl)carboimidoyl dichloride is one of the side products in the case of 3-methylpropioanilide.

3. Reactions with Triphenylphosphine and Dihalogenophosphoranes

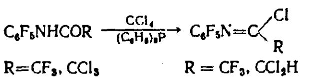
A new convenient method of synthesis of imidoyl chlorides and bromides in high yields has been proposed by Appel and co-workers[104,105] using secondary amides, the corresponding tetrahalogenomethane, and triphenylphosphine as the starting materials:

$$R^1CONHR^2 + (C_6H_5)_3P + CX_4 \rightarrow R^1CX{=}NR^2 + (C_6H_5)_3PO + CHX_3 \quad ;$$
$$R^1 = CH_3, C_6H_5;\ R^2 = C_6H_5,\ cyclo\text{-}C_6H_{11};\ X = Cl, Br \quad .$$

The study of the reaction mechanism suggested that the reaction proceeds via the intermediate *O*-phosphorylated compound formed from the amide on treatment with the complex of the tetrahalogenomethane and triphenylphosphine or the product of their reaction—a dihalogenophosphorane. Taking this into account, a method of synthesis of imidoyl chlorides and bromides from the corresponding dihalogenophosphoranes in the presence of bases (to bind the HHal formed) was developed. The yields of imidoyl halides obtained by this method are also fairly high. The reaction with the less reactive dichlorophosphorane takes place at a higher temperature than the reaction with dibromophosphorane.

The mild conditions in the synthesis of imidoyl chlorides and bromides by this method make it possible to obtain even relatively unstable compounds, which can be used for further reactions without isolation. A convenient version of the reaction has been proposed[106] using triphenylphosphine on a support, which facilitates the separation of phosphorus compounds from imidoyl halides.

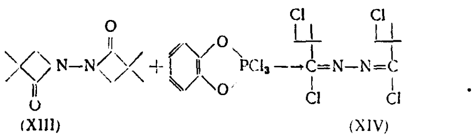
The reaction with triphenylphosphine and CCl_4 has been successfully carried out for trihalogenoacetylpentafluoroanilines in order to synthesise *N*-(pentafluorophenyl)halogenoacetimidoyl chlorides:[107]



$$C_6F_5NHCOR \xrightarrow[(C_6H_5)_3P]{CCl_4} C_6F_5N{=}C\begin{smallmatrix}Cl\\R\end{smallmatrix} \qquad .$$

$$R{=}CF_3, CCl_3 \qquad R = CF_3, CCl_2H$$

NNN'-Substituted ureas[105,108,109] and the *S*-esters of thiocarbamic acid[105] react with CCl_4 and $(C_6H_5)_3P$ like the amides. The dione (XIII) reacts with trichloro-1,2-phenylenedioxyphosphorane and is converted into the azine (XIV) in 70% yield:[110]

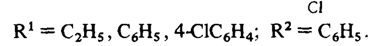


(XIII) (XIV)

IV. REACTIONS OF COMPOUNDS WITH A NITROGEN–CARBON MULTIPLE BOND

1. Reactions of Ketoximes and Aldoximes

Aromatic and aryl-substituted aliphatic ketoximes undergo the Beckmann rearrangement on treatment with CCl_4 and $(C_6H_5)_3P$, affording imidoyl chlorides. The unsubstituted aryl group then migrates in the diaromatic ketoximes, while in aryl-substituted aliphatic ketoximes the aryl group migrates. The yields are in the range 70–90%:[111]

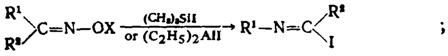


$$(C_6H_5)_3P + CCl_4 + \begin{smallmatrix}R^1\\R^2\end{smallmatrix}{>}C{=}N{-}OH \rightarrow R^1{-}\underset{Cl}{\underset{|}{C}}{=}N{-}R^2 \quad ;$$

$$R^1 = C_2H_5, C_6H_5, 4\text{-}ClC_6H_4;\ R^2 = C_6H_5.$$

Under these conditions, the dialiphatic ketoximes are apparently also converted into imidoyl chlorides, but the latter cannot be isolated.[112] Imidoyl chlorides are likewise obtained in the reactions of ketoximes with dichlorophosphorane in the presence of triethylamine.[111] The intermediate *N*-chloroketimines or their precursors, namely *O*-phosphorylated ketoximes, undergo the Beckmann rearrangement in these reactions.[111]

The Beckman rearrangement of *O*-substituted oxime derivatives on treatment with trimethylsilyl iodide or diethylaluminium iodide in an aprotic medium under mild conditions makes it possible to obtain high yields of imidoyl iodides, which can be used for further reactions with isolation in a pure form:[113]

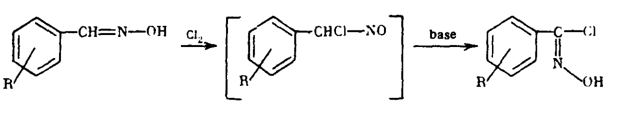


$$\begin{smallmatrix}R^1\\R^2\end{smallmatrix}{>}C{=}N{-}OX \xrightarrow[\text{or } (C_2H_5)_2AlI]{(CH_3)_3SiI} R^1{-}N{=}C\begin{smallmatrix}R^2\\I\end{smallmatrix} \quad ;$$

$$X = COCH_3, COC_6H_5, COOC_2H_5 \quad .$$

Derivatives of acetone, diethyl ketone, acetophenone, cyclohexanone, and cyclododecanone oximes have been investigated in these reactions.

Aldoximes are converted into compounds with the imidoyl chloride group on treatment with various chlorinating agents. The chlorination of benzaldoximes with chlorine in chloroform or methylene chloride, containing an admixture of ethanol or in the presence of triethylamine as the catalyst, makes it possible to obtain benzohydroximoyl chlorides in satisfactory yields.[114–122] The reaction intermediates are chloronitroso-compounds, which isomerise to hydroximoyl chlorides:



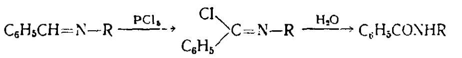
$R = 4\text{-}C_6H_5;\ 4\text{-}NH_2;\ 2,6\text{-}Cl_2;\ H, 3\text{-}NO_2$ and $4\text{-}NO_2;\ 2\text{-}, 3\text{-},$ and $4\text{-}Cl;\ 2,6\text{-}Cl_2.$

The chlorination of pentachlorobenzaldoxime can be achieved without a catalyst. In order to obtain pentafluorobenzohydroximoyl chloride, nitrosyl chloride is used as the chlorinating agent since the reaction hardly occurs with chlorine.

A convenient and selective method of synthesis of benzohydroximoyl chlorides from the corresponding aldoximes on treatment with *N*-chlorosuccinimide has been described.[123,124] Chloral oxime is converted into trichloroacetohydroximoyl chloride on treatment with chlorine.[125]

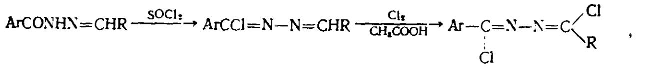
2. Reactions of Aldimines and Aldazines

The formation of imidoyl chlorides has been postulated in the reaction of *N*-benzylideneanilines with PCl_5. Imidoyl chlorides were converted into the corresponding amides without isolation.[126] Satisfactory results have been obtained with *N*-benzylideneaniline, *N*-benzylidene-*p*-toluidine, and *N*-benzylidene-*p*-chloroaniline, but *N*-benzylidene-*p*-nitroaniline could not be made to undergo this reaction:



$$C_6H_5CH{=}N{-}R \xrightarrow{PCl_5} \begin{smallmatrix}Cl\\C_6H_5\end{smallmatrix}{>}C{=}N{-}R \xrightarrow{H_2O} C_6H_5CONHR \quad .$$

Aldazines of the type of 2,3-diazabuta-1,3-diene are converted into monochloro- or dichloro-azines on treatment with chlorine in inert solvents or in anhydrous acetic acid, while their bromination and iodination proceed in a more complex manner. These reactions have been described in detail by Buzykin and co-workers.[12,13] A convenient version of the synthesis of such chlorides involves the interaction of aroylhydrazones with thionyl chloride and subsequent chlorination of the 1-chloro-derivatives formed to 1,4-dichloro-2,3-diazabuta-1,3-dienes [127] [Pilgram and Skiles [128] described the more complex reaction of aroylhydrazones of aliphatic perfluoroaldehydes with $SOCl_2$ in the presence of dimethylformamide (DMF)]:



$$ArCONHN{=}CHR \xrightarrow{SOCl_2} ArCCl{=}N{-}N{=}CHR \xrightarrow[CH_3COOH]{Cl_2} Ar{-}\underset{Cl}{\underset{|}{C}}{=}N{-}N{=}C\begin{smallmatrix}Cl\\R\end{smallmatrix} \quad ,$$

$Ar = C_6H_5, 4\text{-}ClC_6H_4, 4\text{-}CH_3C_6H_4;\ R = C_6H_5, 4\text{-}NO_2C_6H_4, CF_3, C_2F_5, C_3F_7.$

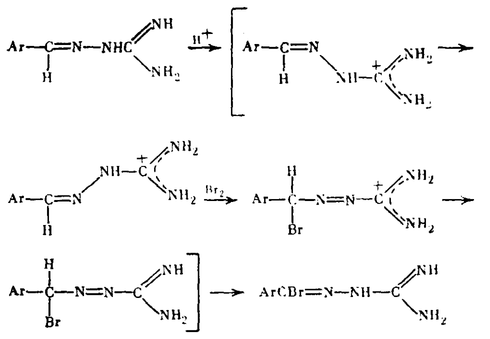
The method makes it possible to obtain the compounds in satisfactory yields and free of isomers, which is especially important for asymmetric derivatives. However, when it is used, one must take into account the symmetrisation side reactions on treatment with $SOCl_2$.[13]

3. Reactions of Hydrazones

New *N*-arylhydrazonobromides have been obtained by the usual methods for the synthesis of compounds of this kind involving treatment with the arylhydrazones of aromatic and aliphatic aldehydes with bromine in acetic acid. The reaction kinetics has been investigated and the role of the electronic steric factors in the formation of the product has been discovered.[12,89,129–131]

N-(Phenyl)trifluoroacetohydrazonobromide and the corresponding chloride can be synthesised in yields up to 70% on halogenation of the phenylhydrazone of trifluoroacetaldehyde with *N*-bromo- and *N*-chloro-succinimide in DMF.[132]

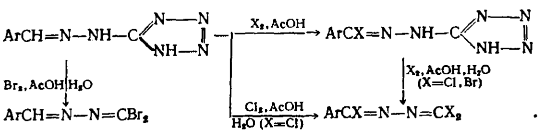
A new group of reactive *N*-amidinohydrazonobromides have been synthesised by brominating amidinohydrazones with bromine in aqueous acetic acid.[133] The compounds were isolated in the form of stable hydrobromides. The kinetic data obtained agree with the reaction mechanism in which the slow rate-determining step is the geometrical isomerisation of the protonated form of the initial thermodynamically stable (*E*)-isomer of the amidinohydrazone to the protonated form of the (*Z*)-isomer followed by the rapid stage involving the bromination of this form:



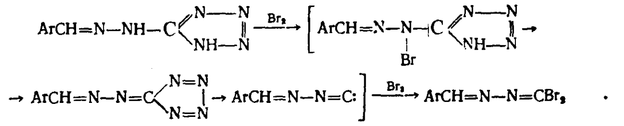
Ar = 4-XC$_6$H$_4$; X = OCH$_3$, CH$_3$, (CH$_3$)$_2$CH, H, Cl, Br.

The formation of hydrazonobromides is also postulated in the bromination of arylidenesemicarbazones with bromine in anhydrous acetic acid, but the final products are triazolones.[134]

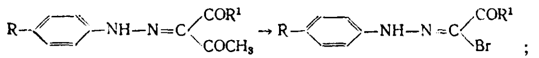
The pathway followed in the reactions of the tetrazolylhydrazones of aromatic aldehydes with chlorine or bromine in acetic acid depends on the conditions.[13] On treatment with halogens in glacial acetic acid, the methylidyne proton of the hydrazone is slowly substituted by the halogen and tetrazolylbenzohydrazonochlorides or the corresponding bromides are obtained respectively. On treatment with halogens in aqueous acetic acid, these compounds undergo oxidative cleavage on the tetrazole ring and are converted into 1,1,4-trihalogeno-2,3-diazabutadienes. Treatment of the initial tetrazolylhydrazones with halogens in aqueous acetic acid also leads to the cleavage of the tetrazole ring. The 1,1-dibromo- and 1,1,4-trichloro-derivatives are then formed in the reactions with bromine and chlorine respectively. The bromination of the 1,1-dibromo-derivative to the 1,1,4-tribromo-derivative does not take place. Thus, in order to obtain the 1,1,4-trihalogeno-derivatives of 2,3-diazadienes, it is necessary that the methylidyne position be halogenated before the cleavage of the tetrazole ring:



The study of the bromination kinetics suggested the following mechanism of the formation of 1,1-dibromo-derivatives:



The bromination of the 5-phenyltetrazolylhydrazones of aromatic aldehydes has been described by Hegarty et al.[135] The attempts to involve ketone tetrazolylhydrazones in the bromination reaction were unsuccessful with the exception of benzophenone tetrazolylhydrazone.[136] On the other hand, *C*-alkoxycarbonyl derivatives of *N*-arylhydrazonobromides have been obtained[137] by brominating hydrazones (XV) in a mixture of glacial acetic acid and acetic anhydride in the presence of sodium acetate:

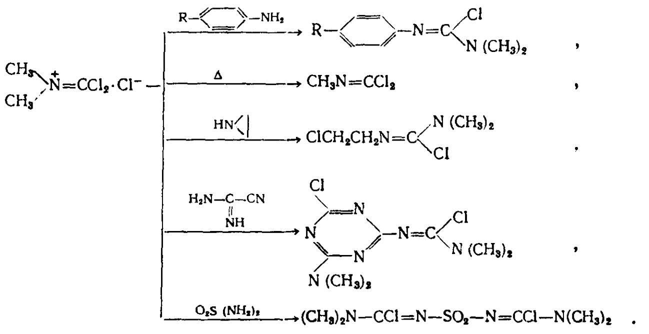


(XV)

R = Br, CH$_3$; R^1 = OC$_2$H$_5$, OCH$_3$.

4. Reactions of Dichloromethyleneammonium Salts

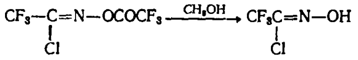
The highly reactive dichloromethyleneammonium salts having the general formula $R_2\overset{+}{N}{=}CCl_2.X^-$, which have been vigorously investigated in recent years, can serve as starting materials in the synthesis of carboimidoyl dichlorides and chlorides. Thus thermolysis of dichloromethylenedimethylammonium chloride above 100 °C leads to *N*-methylcarboimidoyl dichloride and its reaction with compounds containing the amino-group makes it possible to obtain smoothly chloroformamidines:



The reactions of dichloromethyleneammonium salts are described in greater detail in Refs.138–141.

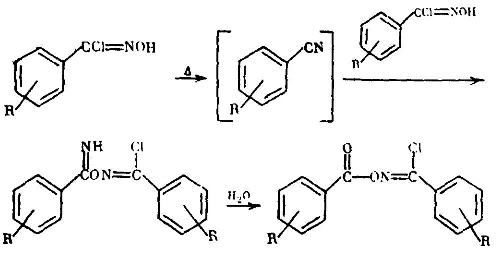
5. Reactions of Imidoyl Halides

For the synthesis of new imidoyl halides, it is possible to use the reactions of the compounds themselves involving the substitution of the halogen atom at the N=C bond, the reactions of other substituents, and also isomerisation not involving the $N{=}\overset{|}{C}{-}Hal$ group. The methods associated with the reactions of the first type have been examined in a review.[142] The reactions of the second type are extremely varied. Thus difluoroacetohydroximoyl chloride can be obtained from *O*-(trifluoroacetyl)trifluoroacetohydroximoyl chloride with methanol.[46–49,143] The reverse reaction makes it possible to synthesise *O*-acylhydroximoyl chlorides from hydroximoyl chlorides:[122,144,145]



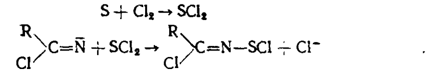
$$\underset{\displaystyle Cl}{CF_3-\overset{|}{C}}=N-OCOCF_3 \xrightarrow{CH_3OH} \underset{\displaystyle Cl}{CF_3\overset{|}{C}}=N-OH$$

Pyrolysis of benzohydroximoyl chlorides containing electron-accepting substituents in the ring leads to O-benzoylbenzohydroximoyl chlorides, but the yields of the products are low.[146] The reaction mechanism involves the reactions of intermediate benzonitriles:



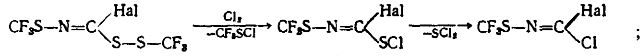
R = 3-NO$_2$, 4-NO$_2$, 4-Cl.

On interaction with sulphur in the presence of a chloride ion donor (tetrabutyl or tetraethyl-ammonium chloride), *N*-chloroformimidoyl chlorides are converted into *N*-chlorothioformimidoyl chlorides.[147] The proposed reaction mechanism is presented below:



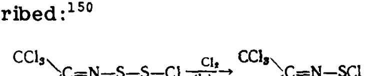
When R = Cl or CCl$_3$, the products can be isolated, but, when R = CN or –CCl$_2$–CN, further reactions take place. *N*-Alkylthio- or *N*-phenylthio-formimidoyl chlorides are formed in the reactions with disulphides.[148] Bis-*N*-chloroformimidoyl chlorides react with disulphides analogously.

The chlorination of *N*-(trifluoromethylthio)trifluoromethyldithioimidoyl fluoride or chloride takes place with cleavage of the S–S bonds:[149]



Hal = F, Cl

Another example of reactions with cleavage of the S–S bond has been described:[150]



N-Chlorocarboimidoyl difluoride reacts via a radical mechanism with fluoro-olefins at a high temperature affording *N*-halogenoalkylcarboimidoyl difluorides.[151,152] The degree of conversion of the initial imidoyl difluoride reaches 75–95%:

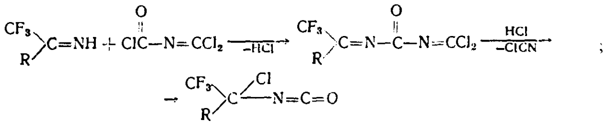
$$ClN{=}CF_2 + CF_2{=}CXF \rightarrow CF_2{=}N{-}CF_2{-}CXFCl \quad ;$$

$$X = F, Cl, Br \quad .$$

The reaction does not take place with hydrogen-containing olefins.

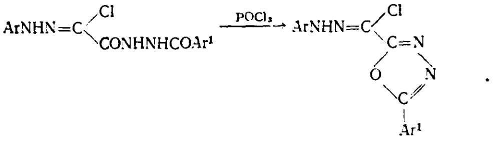
The conversion of *N*-trichloromethylcarboimidoyl dichloride into *N*-chloroformylcarboimidoyl dichloride in a high yield in reactions with aliphatic aldehydes and acid anhydrides has been described.[153]

NN'-Bisalkylideneureas have been isolated in the reactions of ketimines with trichloromethyl isocyanate, which exists preferentially in the form of *N*-chloroformylcarboimidoyl dichloride, under mild conditions in the absence of HCl.[154] In the presence of HCl and on heating, the reaction proceeds further and α-chloroalkyl isocyanates are formed in 75–80% yields:



R = C$_6$H$_5$, 4-ClC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$.

The reaction of a substituent, accompanied by intramolecular cyclisation, has been observed on treating *N*-arylhydrazonochloroacetyl-*N*-benzoylhydrazines with POCl$_3$:[155]



The isomerisation of (*Z*)-isomers of O-alkylbenzohydroximoyl chlorides to the (*E*)-isomers takes place on irradiation with UV light or under the conditions of acid catalysis.[55,56,156]

The reactions of substituents in imidoyl chlorides involving chlorination have been described.[51,52,157] Some examples are presented below:

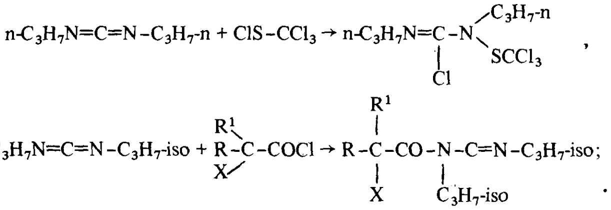
$$CCl_3CCl{=}NCH_2C_6H_5 \xrightarrow{Cl_2} CCl_3CCl{=}NCHClC_6H_5 \quad ,$$

$$RR'C{=}CClN{=}CClC_6H_5 \xrightarrow{Cl_2} RR'CCl{-}CCl_2{-}N{=}CClC_6H_5 \quad ,$$

$$R = H, Br, CH_3CHCCl; \ R'{=}Cl, Br \quad .$$

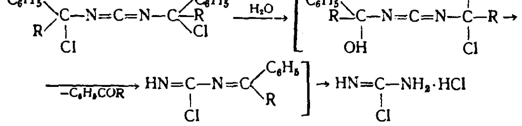
6. Reactions of Carbodiimides

Trichloromethanesulphenyl chloride or α-halogenoacid chlorides add under mild conditions to the C=N bond in carbodiimides affording the corresponding chloroformamidines:[20,158]



X = Cl, Br; R, R^1 = H, CH$_3$

On treatment with water, chloroalkylcarbodiimides are converted into the hydrochloride of chloroformamidine:[159]



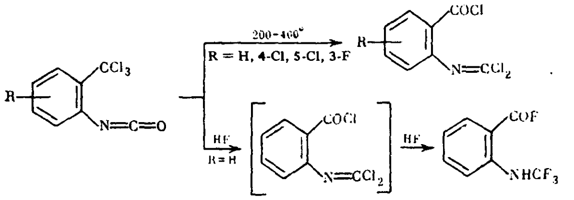
R = CF$_3$, t-C$_4$H$_9$.

Diisopropyl- or dicyclohexyl-carbodiimide reacts with bromodichloromethylphenylmercury, as a source of dichlorocarbene, giving rise to the corresponding carboimidoyl dichloride:[160]

$$R{-}N{=}C{=}N{-}R + C_6H_5HgCCl_2Br \rightarrow RN{=}CCl_2 \quad .$$

7. The Synthesis from Isocyanates and Isothiocyanates

An unusual intramolecular rearrangement with oxygen transfer in a series of o-trichloromethylphenyl isocyanates leads to *N*-phenylcarboimidoyl dichlorides.[161,162] It has been detected in the high temperature thermolysis of these compounds and, in addition, apparently also when the latter were treated with HF:

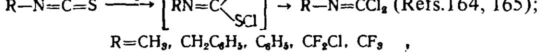


Chloro-1,3-diaza-1,3-dienes can be obtained from perchloroethyl isocyanate and triphenylphosphazo-compounds as a result of the 1,3-chlorotropic shift in the –C–N=C– triad in the carbodiimides formed initially:[94]

$$CCl_3CCl_2N{=}C{=}O + (C_6H_5)_3P{=}NR \rightarrow [CCl_3CCl_2N{=}C{=}N{-}R] \rightarrow CCl_3CCl{=}N{-}CCl{=}NR\ ;\quad R = \text{iso-}C_3H_7,\ C_6H_5.$$

Carboimidoyl dichlorides can be obtained by chlorinating isocyanates or isothiocyanates:

$$SF_5{-}N{=}C{=}O \xrightarrow{PCl_5} SF_5{-}N{=}CCl_2\ \text{(Ref.163)},$$

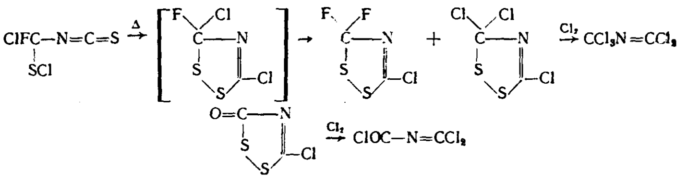


$$R{-}N{=}C{=}S \xrightarrow{Cl_2} \left[RN{=}C\begin{matrix}\diagup Cl\\ \diagdown SCl\end{matrix}\right] \rightarrow R{-}N{=}CCl_2\ \text{(Refs.164, 165)};$$

$$R{=}CH_3,\ CH_2C_6H_5,\ C_6H_5,\ CF_2Cl,\ CF_3\ ,$$

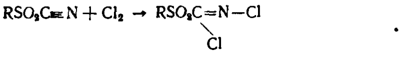
$$F\,(S)\,C{-}N{=}C{=}S \xrightarrow{Cl_2} CFCl_2{-}N{=}CCl_2\ \text{(Ref.165)}.$$

An unusual pathway leading to carboimidoyl dichloride has been discovered in the case of the chloride of chlorofluoroisothiocyanatomethanesulphenic acid.[165] On heating, this compound undergoes intramolecular cyclisation to a 1,2,4-dithiazole derivative. Such dithiazoles or their hydrolysis products afford carboimidoyl dichlorides on treatment with chlorine:



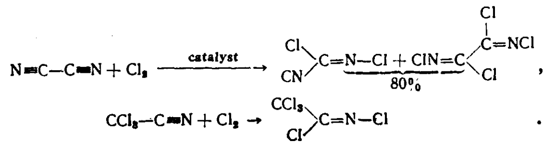
8. Addition to Nitriles, Cyanates, and Isonitriles

A large number of various imidoyl chlorides and dichlorides have been obtained by adding chlorine, sulphenyl chlorides, disulphides, sulphur dichloride, thionyl chloride, and sulphuryl chloride to the C ≡ N bonds of various nitriles. The chlorination of nitriles with electron-accepting substituents leads to substituted *N*-chloroformimidoyl chlorides.[166,167] The addition of chlorine to the activated C ≡ N bond in sulphonyl cyanides takes place readily and with a quantitative yield:



$$RSO_2C{\equiv}N + Cl_2 \rightarrow RSO_2C(Cl){=}N{-}Cl\ .$$

In the case of less activated nitriles, such as, for example, cyanogen or trichloroacetonitrile, the reaction is performed in the presence of catalysts—tetramethylammonium chloride or charcoal:

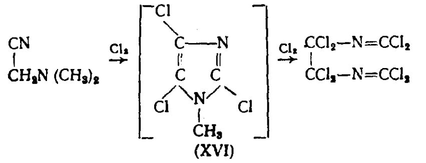


$$N{\equiv}C{-}C{\equiv}N + Cl_2 \xrightarrow{\text{catalyst}} \underbrace{\begin{matrix}Cl\diagdown\\ CN\diagup\end{matrix}C{=}N{-}Cl + ClN{=}C\begin{matrix}\diagup C(Cl){=}NCl\\ \diagdown Cl\end{matrix}}_{80\%}\ ,$$

$$CCl_3{-}C{\equiv}N + Cl_2 \rightarrow \begin{matrix}CCl_3\diagdown\\ Cl\diagup\end{matrix}C{=}N{-}Cl\ .$$

The first stage of the chlorination reaction is nucleophilic attack by the chloride ion on the electron-deficient carbon atom of the cyano-group.

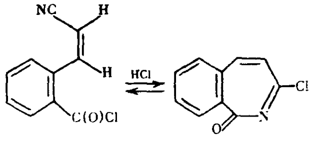
The high-temperature chlorination of dimethylaminoacetonitrile to biscarboimidoyl dichloride (XVI) proceeds via the intermediate formation of an *N*-methylimidazole derivative and subsequent ring opening:



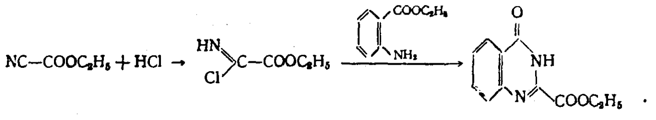
(XVI)

The reactions of nitriles with chloro-derivatives of sulphur proceed in the presence of catalysts (sources of chloride ions) and make it possible to obtain sulphur-containing imidoyl chlorides and dichlorides.[148,149,168–171]

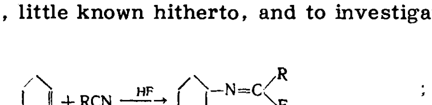
Cyclic imidoyl chlorides are formed in satisfactory yields in the reactions involving the addition of HCl to nitriles, accompanied by intramolecular cyclisation,[172] for example:



The interaction of ethyl cyanoformate and HCl in acetic acid leads to the unstable ethoxycarbonylformimidoyl chloride, which has been detected from the presence of products of its reactions with nucleophiles added to the system. Ethyl 4-quinazolone-2-carboxylate has been obtained in this way in 50% yield in the presence of *o*-ethoxycarbonylaniline:[173]



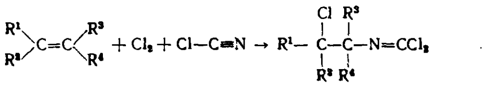
The Ritter condensation of nitriles with olefins in the presence of HF led to imidoyl fluorides, which were isolated in a pure form.[174,175] This reaction made it possible to obtain imidoyl fluorides, little known hitherto, and to investigate their properties:



R=CH₃ (33%), C₆H₅ (59%)

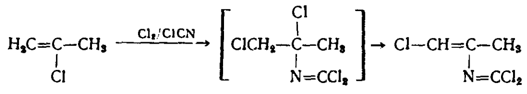
The use in these reactions of not only cyclic but also linear olefins with branched and unbranched chains at the C=C bond showed that alkenes with branched alkyl groups do not form imidoyl fluorides, while those with unbranched groups react normally. For example, pent-1-ene reacts with benzonitrile to form a mixture of *N*-(2-pentyl)benzimidoyl fluoride and the corresponding 3-pentyl derivative in 62% yield. The different behaviour in these processes of the two types of olefins is determined by the possibility of further reactions of the ions formed as intermediates in the addition of HF to olefins.

A preparative method of synthesis of aliphatic *N*-(β-chloroalkyl)carboimidoyl dichlorides consists in the electrophilic addition of chlorine to olefins in the presence of chlorocyanogen:[176]



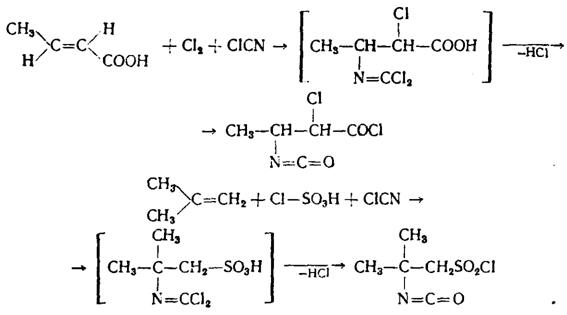
$$\begin{matrix}R^1\diagdown\\ R^2\diagup\end{matrix}C{=}C\begin{matrix}\diagup R^3\\ \diagdown R^4\end{matrix} + Cl_2 + Cl{-}C{\equiv}N \rightarrow R^1{-}\overset{Cl}{\underset{R^2}{C}}{-}\overset{R^3}{\underset{R^4}{C}}{-}N{=}CCl_2$$

Especially satisfactory yields have been obtained with vinyl chloride or butadiene. When α-halogenocarboimidoyl chlorides are formed, dehydrohalogenation, which takes place readily, makes it possible to obtain at once αβ-unsaturated carboimidoyl dichlorides:



$$H_2C{=}C(Cl){-}CH_3 \xrightarrow{Cl_2/ClCN} \left[ClCH_2{-}C(Cl)(N{=}CCl_2){-}CH_3\right] \rightarrow Cl{-}CH{=}C(N{=}CCl_2){-}CH_3$$

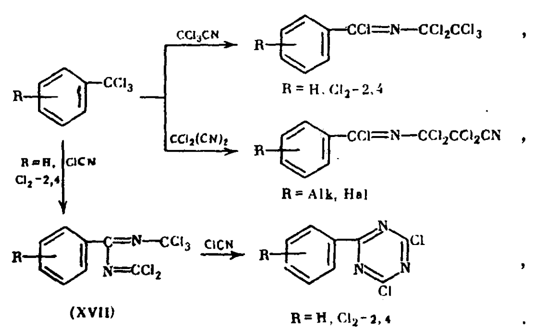
However, in those cases where the olefin contains an acid group or an electrophile capable of introducing such groups is used, the reaction does not stop with formation of carboimidoyl dichloride:



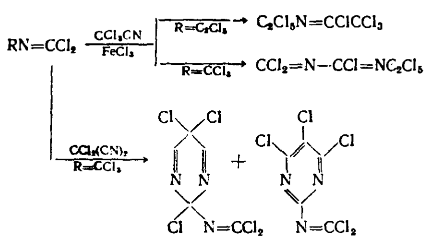
$$CH_3CH{=}CHCOOH + Cl_2 + ClCN \rightarrow \left[CH_3{-}CH(N{=}CCl_2){-}CH(Cl){-}COOH\right] \xrightarrow{-HCl} CH_3{-}CH(N{=}C{=}O){-}CH(Cl){-}COCl$$

$$(CH_3)_2C{=}CH_2 + Cl{-}SO_3H + ClCN \rightarrow \left[CH_3{-}C(CH_3)(N{=}CCl_2){-}CH_2{-}SO_3H\right] \xrightarrow{-HCl} CH_3{-}C(CH_3)(N{=}C{=}O){-}CH_2SO_2Cl$$

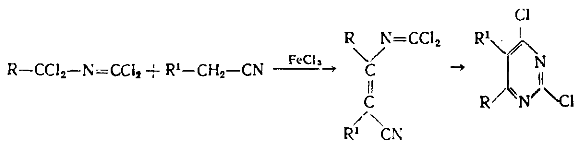
N-Polychloroalkylimidoyl chlorides or dichlorides are formed on interaction of activated nitriles, such as chlorocyanogen, trichloroacetonitrile, 2,2,3-trichloropropionitrile, and dichloromalonidinitrile with compounds having the CCl_3 or CCl_2H groups.[177,178] The reactions are catalysed by $FeCl_3$ or $AlCl_3$. The addition of chlorine-containing compounds to the activated nitrile group takes place in the first stage and is followed by the migration of chlorine (chlorotropism), which results in the formation of imidoyl chlorides or dichlorides. In a number of instances at low temperatures, the processes can be arrested at this stage. In other cases the formation of heterocyclic compounds is observed. Thus imidoyl chlorides are the main products of the reaction of dichloroacetonitrile with trichloromethylbenzenes,[177] but in the reaction with chlorocyanogen cyclisation to substituted triazines takes place readily and the intermediate carboimidoyl dichloride (XVII) could be isolated in small amounts only in the case of 2,4-dichloro-1-trichloromethylbenzene:[178]



Imidoyl chlorides have also been isolated in the reactions of trichloromethylbenzenes with dichloromalonodinitrile,[177] while the reaction with benzylidenechloro-derivatives gave rise to pyrimidine derivatives.[178] Trichloromethoxybenzenes and carboimidoyl dichlorides with perchloroalkyl groups have also been used as the polychloroalkyl component:[177–179]

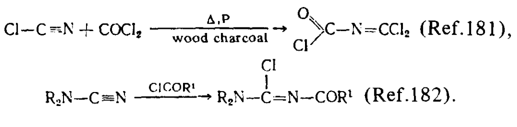


It has also been found that, in the presence of Lewis acids and at elevated temperatures, carboimidoyl dichlorides of the type $RCCl_2N{=}CCl_2$ react with nitriles having two hydrogen atoms in the α-position, affording chloropyrimidines.[180] The elimination of HCl is rate determining in this two-stage reaction. In most cases the reaction can be stopped at the first stage involving the formation of carboimidoyl dichloride:



R=Cl, CCl_3, C_6H_5; R^1=H, Cl, CH_3, C_6H_5 etc.

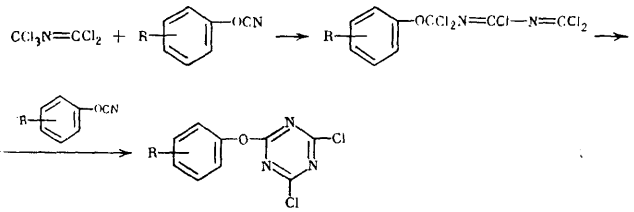
The reaction proceeds analogously also when the α-chlorine atoms in carboimidoyl dichloride have been substituted by hydrogen and the α-hydrogen atoms of the nitrile have been substituted by chlorine. *N*-Acylimidoyl chlorides and dichlorides can be obtained from nitriles and acyl chlorides:



$$Cl{-}C{\equiv}N + COCl_2 \xrightarrow[\text{wood charcoal}]{\Delta,P} \overset{O}{\underset{Cl}{>}}C{-}N{=}CCl_2 \quad \text{(Ref.181)},$$

$$R_2N{-}C{\equiv}N \xrightarrow{ClCOR^1} R_2N{-}C(Cl){=}N{-}COR^1 \quad \text{(Ref.182)}.$$

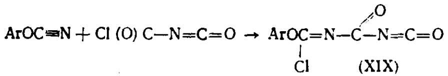
Like nitriles, phenyl isocyanates react with *N*-trichloromethylcarboimidoyl dichloride, giving rise to heterocyclic derivatives.[178] In some cases it is possible to isolate small amounts of the primary products of the chlorotropic rearrangement:



R = H, Cl-4, Cl_2-2,4, $(CH_3)_2$-2,4

Cyanates react with acyl chlorides similarly to nitriles.[182] The reaction is carried out by heating in inert solvents, the yield of products being 45–90%. Phosgene reacts at 0–20 °C.

The electrophilic addition of chloroformyl isocyanate to aromatic cyanates leads to compounds of type (XIX):[181,183]

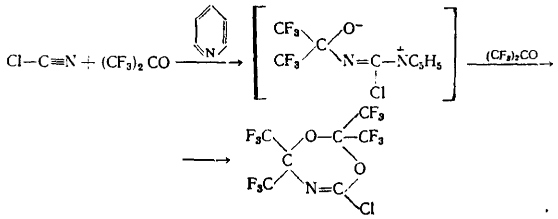


$$ArOC{\equiv}N + Cl(O)C{-}N{=}C{=}O \rightarrow ArOC(Cl){=}N{-}C({=}O){-}N{=}C{=}O$$

(XIX)

Ar = C_6H_5, 4-$CH_3C_6H_4$, 4-ClC_6H_4.

The interaction of chlorocyanogen with hexafluoroacetone in the presence of pyridine results in the formation of chlorodioxazine:[184]

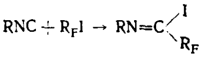


N-Bromocarboimidoyl difluoride has been obtained by brominating fluorocyanogen in the presence of alkali metal fluorides:[185]

$$FC{\equiv}N + Br_2 \xrightarrow{MF} [CF_2{=}\overset{-}{N}\,\overset{+}{M}] \xrightarrow{Br_2} CF_2{=}N{-}Br$$
$$M{=}K,\ Cs,\ Rb$$

It has been suggested that *N*-pentafluorotelluroimidoyl chloride and dichloride be obtained by the photolysis of chlorocyanogen or trifluoromethylcyanogen with TeF_5Cl. Up to 10% of tetrachloro-2,3-diazabuta-1,4-diene is then obtained as a side product.[186]

The radical addition of perfluoroalkyl iodides to isonitriles with primary or secondary alkyl groups is a method of synthesis of imidoyl iodides with perfluoroalkyl groups:[187,188]



$$RNC + R_FI \rightarrow RN{=}C(I)R_F$$
$$R = n\text{-}C_4H_9,\ cyclo\text{-}C_6H_{11};\ R_FCF_3(CF_2)_n\ (n = 3, 5, 7).$$

However, there is no condensation with t-alkyl or aromatic isonitriles under these conditions. By carrying out the reactions in the presence of copper, it has been possible to involve in them also the nitriles indicated above. The yields of imidoyl iodides are mainly 70–90%. The mechanism of the copper-catalysed reaction involves the oxidative addition of R_FI to the copper complex of the isonitrile and the subsequent migration of the perfluoroalkyl group and iodine to the isonitrile ligand.

Direct fluorination of isonitriles by a stream of elemental fluorine diluted with argon or nitrogen makes it possible to obtain carboimidoyl difluoride:[189]

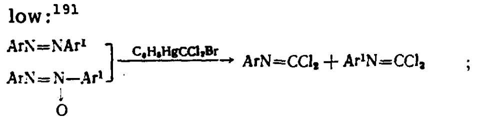
$$RNC + F_2 \rightarrow RN{=}CF_2\quad,$$
$$R = t\text{-}C_4H_9,\ C_6H_5,\ 2\text{-}FC_6H_4,\ 4\text{-}ClC_6H_4.$$

N-Trifluoromethylimidoyl halides are formed in the reactions of *N*-trifluoromethylisonitrile with HHal or SF_5Br.[190]

V. REACTIONS OF COMPOUNDS WITH A NITROGEN–NITROGEN MULTIPLE BOND

Azides, azo-compounds, and azoxy-compounds react with dichlorocarbene, generated in the course of the reaction from phenyltrihalogenomethylmercury, giving rise to carboimidoyl dichlorides.[191,192] Thus the decomposition of phenyl azide in the presence of phenyltrichloromethylmercury leads to *N*-phenylcarboimidoyl dichloride in 70% yield. Sodium trichloroacetate or ethyl trichloroacetate can also serve as a source of dichlorocarbene. The reaction kinetics has been investigated for phenyl, p-methoxyphenyl, and p-chlorophenyl azides.[192]

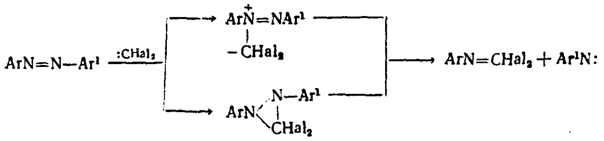
The reaction of an excess of azo- and azoxy-benzenes with bromodichloromethylphenylmercury results in the formation of a mixture of the same carboimidoyl chlorides. The azoxy-compounds are apparently initially deoxygenated by the organomercury derivative and the resulting azobenzenes react with dichlorocarbene. The overall yield of the products is low:[191]



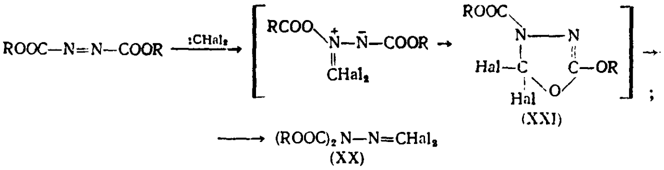
$$\left.\begin{array}{l} ArN{=}NAr^1 \\ ArN{=}N(\rightarrow O){-}Ar^1 \end{array}\right] \xrightarrow{C_6H_5HgCCl_2Br} ArN{=}CCl_2 + Ar^1N{=}CCl_2\quad;$$

$$Ar = C_6H_5,\ 4\text{-}ClC_6H_4,\ 4\text{-}CH_3C_6H_4;\ Ar^1 = C_6H_5,\ 4\text{-}ClC_6H_4.$$

The mechanism of the formation of carboimidoyl dichloride can include the participation of open-chain or cyclic intermediates, for example:



The reaction of trihalogenomethylmercury derivatives with aliphatic azo-compounds proceeds differently.[193] Depending on the mercury compound, azodicarboxylate esters afford dichloro-, dibromo-, or bromochloro-derivatives of compound (XX):

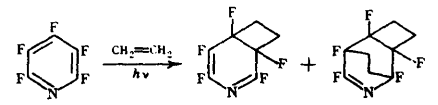


R=CH₃, C₂H₅; Hal=Cl, Br .

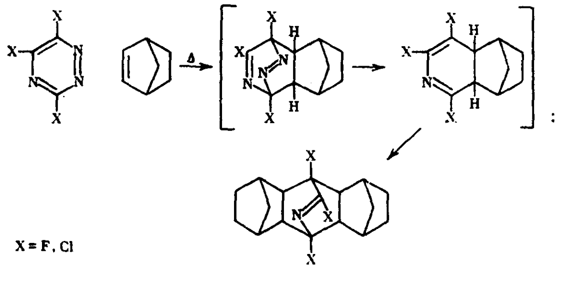
The reaction begins with the electrophilic attack by the nitrogen atom on the dihalogenocarbene with subsequent formation of intermediate 1,3,4-oxadiazolines (XXI), which have been detected spectroscopically.

VI. REACTIONS OF COMPOUNDS WITH A CARBON–CARBON MULTIPLE BOND

Compounds with the imidoyl chloride or imidoyl fluoride groups incorporated in a ring are formed in the photochemical Diels–Alder addition of unsaturated hydrocarbons to nitrogen-containing heterocycles. Thus the reactions of pentafluoropyridine with linear and cyclic olefins and also with acetylenic derivatives give rise to 1:1 and 2:1 adducts containing the imidoyl fluoride group:[194–196]



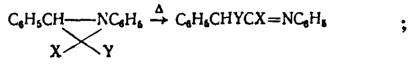
The thermal reactions of 3,5,6-trifluoro- or 3,5,6-trichloro-1,2,4-triazines with olefins proceed in a more complex manner, but in this case too the products are compounds with a halogenoimidoyl group,[197] for example:



X = F, Cl

VII. THERMOLYSIS OF 3,3-DIHALOGENOAZIRIDINES

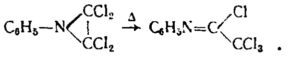
3,3-Dihalogeno-1,2-diphenylaziridines are converted into *N*-phenylimidoyl halides in various solvents at 80–100 °C:[198]



$X=Y=Cl, Br; X=Cl, Y=Br; X=F, Y=Br; X=F, Y=Cl$.

This thermal isomerisation involves the 1,2-migration of the halogen and the dissociation of the adjoining C–N bond with the opening of the aziridine ring. The study of the reaction kinetics and analysis of the calculated data made it possible to establish the reaction mechanism. The series based on the capacity of the halogens for migration, namely Br > Cl > F, found is consistent with the C–Hal bond energies. The rate of isomerisation depends not only on the nature of the migrating halogen but also on the halogen which remains. Fluorine significantly facilitates migration compared with chlorine and bromine.

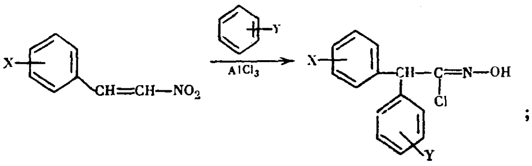
The yields of the imidoyl halides are fairly high. 3,3-Dibromo-1,2-diphenylaziridine is thermally less stable than the corresponding dichloro-derivative. Tetrachloroaziridines are thermally more stable than dichloroaziridines, but at 180 °C the two isomerise to imidoyl chlorides:[191]



The rearrangement of tetrachloro-*N*-isopropylaziridine does not take place even on prolonged heating.

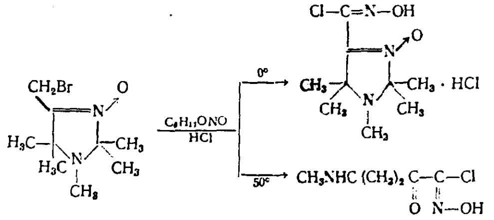
VIII. OTHER METHODS

New diarylacetohydroximoyl chlorides have been obtained by the reaction, already known previously, of β-nitrostyrenes with aromatic hydrocarbons in the presence of Lewis acids, which proceeds via 1,4-addition to the conjugated nitro-olefin chain:[199,200]

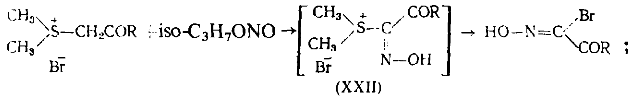


$X = 2\text{-Br};\ 2,4\text{-Cl}_2;\ 2,6\text{-Cl}_2; 2\text{-Cl}, 6\text{-F};$
$Y = H, 4\text{-CH}_3, 4\text{-C}_2H_5, 4\text{-iso-C}_3H_7, 4\text{-Br}, 4\text{-F}, 4\text{-Cl}.$

The reactions of β-nitrostyrenes with acetyl chloride form under these conditions, together with other products, *N*-acetoxyphenylchloroacetotrihydroximoyl chlorides, whose yield depends significantly on the Lewis acid employed (it is a maximum for $TiCl_4$) and the substituents in the nitrostyrene molecule.[201,202] In the reaction with benzoyl chloride in the presence of triethylamine, trifluoronitroethane is converted into trifluoroacetohydroximoyl chloride (yield 30%).[203] Certain heterocyclic hydroximoyl chlorides have been obtained by the conversion of the corresponding halogenomethyl derivatives into oximes by treatment with isopentyl nitrite in hydrochloric acid.[204,205] In a series of 3-imidazoline 3-oxides, the formation of the hydroximoyl chloride at an elevated temperature is accompanied by the opening of the heterocyclic ring:



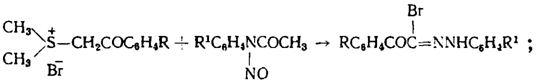
Hydroximoyl bromides have been obtained in satisfactory yields by the reactions of isopropyl nitrite with sulphonium bromides.[206] Under these conditions, the salt (XXII) is apparently formed initially and then undergoes intramolecular nucleophilic substitution by the bromide ion with formation of a sulphide:



$R=C_6H_5, CH_3, OC_2H_5$.

The nitrosation of dimethylphenylacylsulphonium bromide with sodium nitrite and HCl in aqueous dioxan leads to benzoylhydroximoyl chloride, also in a high yield.[207] Similar chlorides are formed effectively also in the nitrosation of β-ketosulphoxides with sodium nitrite in HCl, which is a fairly convenient and general method of synthesis of hydroximoyl chlorides of this kind.[208]

The azo-coupling reaction between sulphonium bromides and *N*-nitrosoacetanilides, which is similar to their nitrosation reaction, in non-aqueous solvents leads to hydrazonobromides:[209]

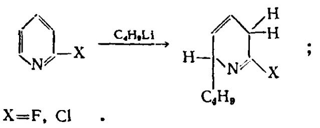


$$(CH_3)_2\overset{+}{S}\text{–}CH_2COC_6H_4R\ \bar{Br} + R^1C_6H_4N(NO)COCH_3 \rightarrow RC_6H_4COC(Br){=}NNHC_6H_4R^1\ ;$$

$R = H, 4\text{-CH}_3, 4\text{-Br}, 4\text{-NO}_2;\ R^1 = H, 4\text{-CH}_3, 4\text{-OCH}_3, 4\text{-Cl}.$

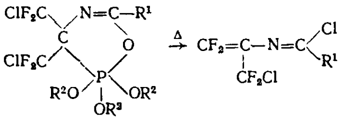
Imidoyl fluorides and difluorides are also formed in the photolysis of various polyfluoro-compounds. Thus perfluoroimidoyl fluorides and difluorides with a linear structure have been obtained in this way from perfluoroaza- and perfluorodiaza-cyclohexadienes;[210] *N*-(1-Chloro-octafluorobutyl)carboimidoyl difluoride has been obtained in 22% yield from *N*-chloroperfluoropiperidine.[211] The low-temperature photolysis of 1-adamantyl nitrite in the presence of trichloronitrosomethane results in the formation of up to 5% of *N*-[*O*-(1-adamantyl)]carboimidoyl chloride, which was isolated and characterised.[212]

Relatively unstable cyclic imidoyl fluorides and chlorides are formed from 2-fluoro and 2-chloro-pyridines by their reaction with butyl-lithium:[213]



X=F, Cl .

The thermolysis of 2,3-dihydro-1,4,2,λ^5-oxazaphosphole derivatives leads to reactive *N*-vinylimidoyl chlorides:[214]



$R^1 = t\text{-}C_4H_9, C_6H_5, 4\text{-}CH_3C_6H_4, 4\text{-}ClC_6H_4, CH{=}CH\text{-}C_6H_5$; $R^2 = CH_3, C_6H_5$.

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During the preparation of the manuscript for printing, new data were published on the synthesis of various compounds with halogenoimidoyl groups or on their formation as intermediates. Most of these communications are concerned with the reactions of nitriles and isonitriles with acyl halides,[215-219] sulphenyl chlorides or sulphur dichloride,[220-222] and the halogens (chlorine and bromine) in the presence of mercury difluoride,[223] and also with the reactions of amide groups on treatment with PCl_5.[224-227] Halogenoimidoyl derivatives have also been obtained or have been postulated in the chlorination of aldoximes,[228] in the interaction of perhalogenoalkylamines with SbF_5 [229] or in their thermolysis,[223] in the reactions of substituents in compounds already containing the halogenoimidoyl group,[222,230] and in certain other reactions.[231-237]

The main trend in these investigations has been the study of the configurations of different halogenoimidoyl groups by spectroscopic methods and the synthesis of the individual isomers and their interconversions.[228,237-239]

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Pyrido[2,3-*d*] pyrimidines

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The methods of synthesis and the chemical and biological properties of pyrido[2,3-*d*] pyrimidines are described. The bibliography includes 270 references.

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I. INTRODUCTION

In recent years investigators have shown much interest in pyrido[2,3-*d*]pyrimidines—heterocyclic systems with a broad spectrum of biological properties[1–4] some of which have found applications in medicine as medicinal preparations.[5,6] Only one review has been published on the synthesis of pyrido[2,3,d]pyrimidines, covering the literature data up to 1968[7] including also recent information about their chemical reactions and biological properties.

As a result of the theoretical and practical interest in pyrido[2,3-*d*]pyrimidines, many publications devoted to new methods of synthesis, chemical reactions, and biological properties of compounds of this class have appeared during the last 15 years, so that it is of interest to survey and treat systematically the available literature data.

II. METHODS OF SYNTHESIS

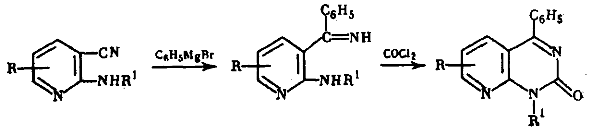
Condensed pyridopyrimidines can be synthesised from both pyridine and pyridimine derivatives.

1. Synthesis from Pyridines

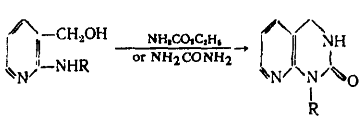
This section deals with the synthesis of pyrido[2,3-*d*]-pyrimidines with various functions group substituents in the pyrimidine ring from pyridines containing active groups in the 2- and 3-positions, which interact with the corresponding reactants, the reaction leading to closure of the pyrimidine ring.

(a) *2-Oxo-derivatives*

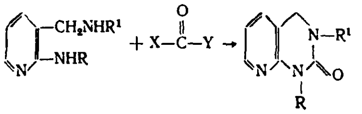
2-Oxo-4-phenyl-1,2-dihydropyrido[2,3-*d*]pyrimidines have been synthesised from 2-amino-2-cyanopyridines by reaction with a Grignard reagent and then with phosgene:[8–10]



Another method consists of the condensation of 2-amino-3-benzoylpyridines with urethane[9] or urea.[11] Under analogous conditions, 2-amino-3-hydroxymethyloyridines cyclise to the corresponding oxotetrahydropyrido[2,3-*d*]-pyrimidines:[12]

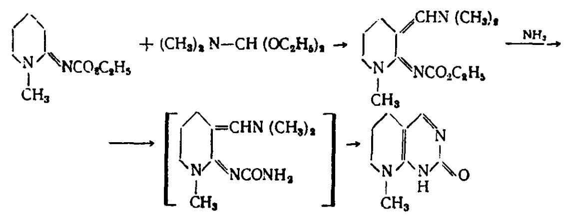


Analogues of these compounds containing substituents in the 3-position in the pyridine ring have been obtained by condensing 2-amino-3-aminomethylpyridines with various carbonic acid derivatives:[13]



X = halogen, alkoxy-group, amino-group; Y = halogen, alkoxy-group, trihalogenoalkyl.

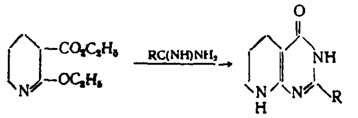
2,2-Dialkoxy-2-methylpiperidine has been used to synthesise *N*-methyl-2-oxohexahydropyridopyrimidines by its condensation with urethane to form an amidine. The reaction of the latter with dimethylformamide acetal yielded aminomethylene-ethoxycarbonyliminopiperidine whose treatment with aqueous ammonia led to the closure of the pyrimidine ring with the simultaneous elimination of dimethylamine:[14]



2-Oxodihydropyrido[2,3-*d*]pyrimidines have also been obtained by condensing 3-acetyl-2-pyridones with urea.[15]

(b) *4-Oxo-derivatives*

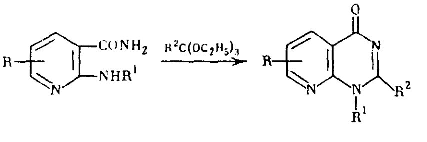
Methods of synthesis of 2-substituted 4-oxo-3,4,5,6,7,8-hexahydropyrido[2,3-d]pyrimidines from 3-ethoxycarbonyl-2-ethoxy-3,4,5,6-tetrahydropyridine have been developed:[16]



R=NH₂, CH₃

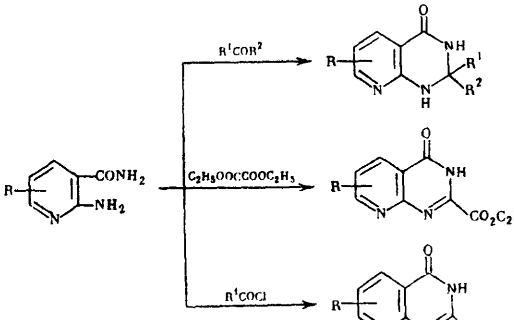
The methods of synthesis of analogous pyridopyrimidines containing alkyl groups at the nitrogen atom of the piperidine ring[17,18] and an angular substituent in the 10-position[16] have also been investigated.

2-Amino-3-carbamoylpyridines, whose condensation with orthoesters leads to the closure of the pyrimidine ring, are convenient starting materials for the synthesis of 1-substituted 4-oxo-1,4-dihydropyrido[2,3-d]pyrimidines:[19-25]

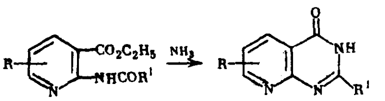


R²=H, alkyl, phenyl

The reactions of 2-amino-3-carbamoylpyridines with aldehydes or ketones,[26] diethyl oxalate,[29] and acid chlorides[30] result in the formation of the corresponding 4-oxopyridopyrimidines:

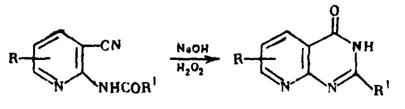


On treatment with alcoholic ammonia, 2-acylamino-3-ethoxycarbonylpyridines cyclise to form 2-substituted 4-oxodihydropyrido[2,3-*d*]pyrimidines:[30-32]

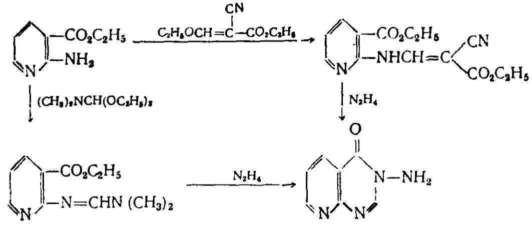


The hydrochlorides of various amines are used instead of ammonia as the cyclising agents for the synthesis of 2,3-substituted 4-oxodihydropyridopyrimidines from acylaminopyridines and the reaction is carried out in the presence of phosphorus pentoxide.[33]

2-Acylamino-3-cyanopyridines undergo an interesting reaction with sodium hydroxide and hydrogen peroxide, which yields 4-oxodihydropyridopyrimidines:[34,35]

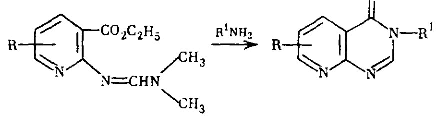


3-Amino-4-oxodihydropyrido[2,3-*d*]pyrimidine has been synthesised by condensing 2-amino-3-ethoxycarbonylpyridine with ethyl ethoxymethylenecyanoacetate or dimethylformamide acetal, this being followed by treating the intermediates with hydrazine hydrate:[36]

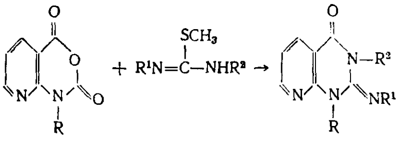


The reaction of 2-amino-3-hydrazinocarbonylpyridine with dimethylformamide diacetal gives an analogous result.[37]

On treatment of *N*-(2-pyridyl)amidines with various amines, intramolecular cyclisation takes place with formation of 3-substituted 4-oxodihydropyrido[2,3-*d*]pyrimidines:[38]

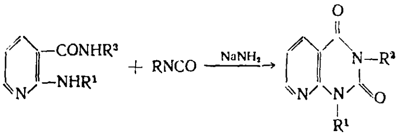


The reaction of thiourea derivatives with 1-substituted 2,4-dioxo-1,2-dihydro-4*H*-pyrido[2,3-d]1,3-oxazines, obtained by condensing aminopyridines with phosgene, has been used to synthesise various derivatives of 4-oxopyridopyrimidines:[39,40]



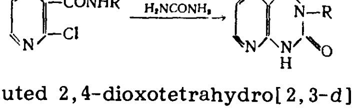
(*c*) 2,4-Dioxo-derivatives

One of the commonest methods of synthesis of 1,3-disubstituted 2,4-dioxotetrahydropyrido[2,3-*d*]pyrimidines is the condensation of derivatives of 2-amino-3-carbamoylpyridines with isocyanates in the presence of sodium amide:[41-45]

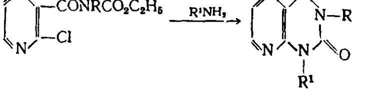


Analogous compounds have been obtained by cyclising aminocarbamoylpyridines with phosgene, chlorocarbonic acid ester or amide, and urea.[46-51]

The interaction of 2-chloro-3-carbamoylpyridines with urea afforded high yields of 3-substituted 2,4-dioxotetrahydropyridopyrimidines:[52,53]

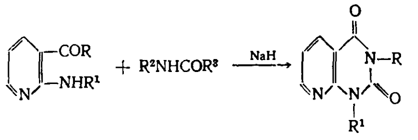


1,3-Disubstituted 2,4-dioxotetrahydro[2,3-*d*]pyrimidines can be synthesised from derivatives of 2-chloro-3-carbamoylpyridines containing the ethoxycarbonyl group at the nitrogen atom in the amide group condensing with amines:[54]



The synthesis of 1,3-disubstituted pyridopyrimidines from 2-chloro-3-carbamoylpyridines and isocyanates has been described.[55]

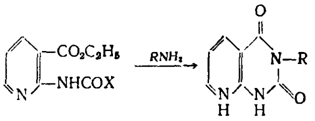
The corresponding 1,3-disubstituted dioxopyrimidines have been synthesised by condensing 3-substituted 2-halogeno-carbamoylpyridines with carbamates in the presence of sodium hydride in dimethylformamide (DMF).[56] The interaction of the same carbamates with 2-amino-3-ethoxycarbonyl- or 2-amino-3-carbamoyl-pyridines results in the formation of analogous pyridopyrimidines with a different disposition of the substituents in the pyrimidine ring—in the 1- and 3-positions:[57]



$R=OC_2H_5$, NH_2; R^3=halogen, heterocycle.

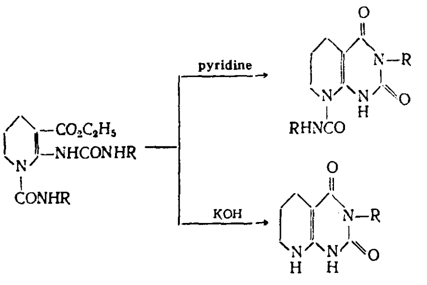
One of the ways of synthesising 2,4-dioxopyrido[2,3-*d*]-pyrimidines is condensation of 2-amino-3-carboxy- or 2-amino-3-ethoxycarbonyl-pyridines with urea, urethanes, or isocyanates.[58–65]

It has been shown that refluxing of 2-amino-3-ethoxycarbonylpyridine with chlorocarbonic esters or amide leads to the formation of 2-alkoxycarbonylamino- or ureido-derivatives of pyridine, which cyclise on treatment with amines to the corresponding dioxopyridopyrimidines:[66]

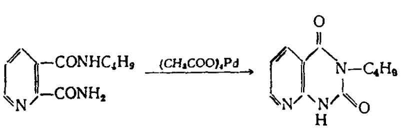


X = alkoxy-group, NH_2.

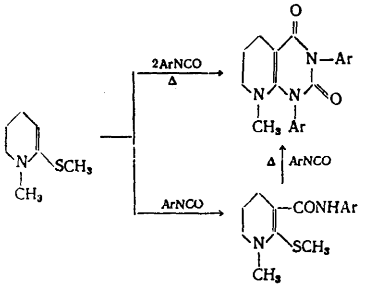
The interaction of 2-amino-3-ethoxycarbonyl-1,4,5,6-tetrahydropyridine with isocyanate yielded diureido-derivatives which cyclise in the presence of pyridine or potassium hydroxide to the corresponding 2,4-dioxo-octahydropyridopyrimidines:[67]



A novel method of synthesis of 3-butyl-2,4-dioxotetrahydropyrido[2,3-d]pyrimidine involves the refluxing of 2,3-dicarbamoylpyridine in DMF in the presence of palladium tetra-acetate:[68]



Single-stage and two-stage syntheses of 1,3-diaryl-2,4-dioxo-octahydropyridopyrimidines from 1-methyl-2-methylthiotetrahydropyridine and aryl isocyanates in accordance with the scheme

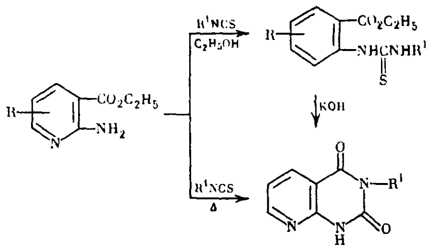


have been proposed.[69,70] The use of aryl isothiocyanates makes it possible to obtain the corresponding 2,4-dithiono-derivatives.[71]

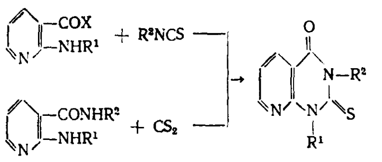
2,4-Dioxopyridopyrimidines can also be synthesised from dioxopyrido[2,3-d]-1,3-oxazine by treatment with amines and phosgene.[72,73]

(*d*) *4-Oxo-2-thionopyrido[2, 3-d]pyrimidines*

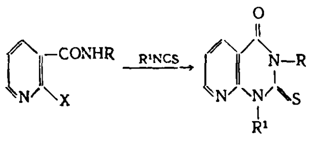
One of the convenient methods of synthesis of 4-oxo-2-thionotetrahydropyrido[2,3-*d*]pyrimidines involves the thermal cyclisation of 3-alkoxycarbonyl-2-aminopyridines by reaction with isothiocyanates with or without the isolation of the intermediate thioureidopyridines:[74–78]



1,3-Disubstituted compounds have been obtained from the esters or amides of 2-aminopyridine-3-carboxylic acids and various isothiocyanates[79] or carbon disulphide:[80,81]

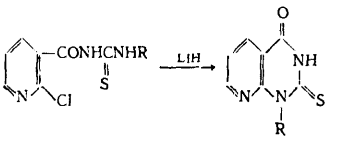


Analogous pyridopyrimides have been obtained by the reaction of 3-carbamoylpyridines, containing halogeno-, alkoxy-, alkylthio-, and sulphoxy-groups in the 2-position in the pyridine ring, with isothiocyanates:[82–84]



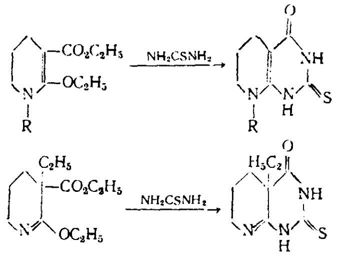
When 2-chloro-3-ethoxycarbonylpyridines are refluxed with thiourea derivatives in ethanol saturated with hydrogen chloride, the corresponding pyridopyrimidines are formed in low yields.[85–87]

1,3-Disubstituted 4-oxo-2-thionotetrahydropyridopyrimidines have been synthesised by cyclising 2-chloroicotinoylthioureas in the presence of lithium hydride:[88]



1,3-Diaryl-8-methyl-4-oxo-2-thiono-1,2,3,4,5,6,7,8-octahydropyrido[2,3-d]pyrimidines have been obtained by the reaction of 3-arylcarbamoyl-1-methyl-2-methylthiotetrahydropyridine with aryl isothiocyanate.[69]

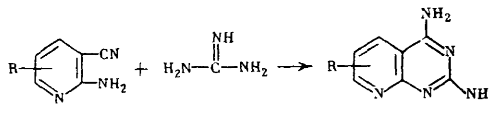
The esters of the lactim form of 3-ethoxycarbonylpiperidin-2-ones are convenient starting compounds for the synthesis of various pyrido[2,3-*d*]pyrimidines which cannot be synthesised in other ways:[16–18]



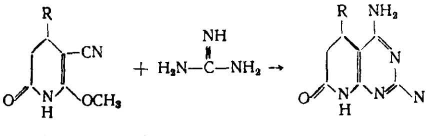
The synthesis of 4-imino-1,3-dimethyl-2-thionotetrahydropyrido[2,3-d]pyrimidine by condensing 2-chloro-3-cyanopyridine with *NN*′-dimethylthiourea has been reported.[89]

(e) *2,4-Diaminopyrido[2,3-d]pyrimidines and Other Derivatives*

2-Amino-3-cyanopyridines readily react with guanidine to form derivatives of 2,4-diaminopyrido[2,3-*d*]pyrimidines:[90,91]

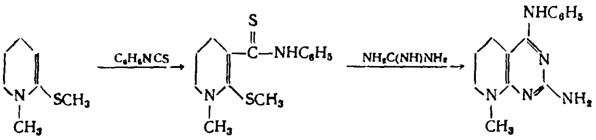


Another method of synthesis of 2,4-diaminopyridopyrimidines involves the reaction of 3-cyano-2-methoxypyridines with guanidine:[92]

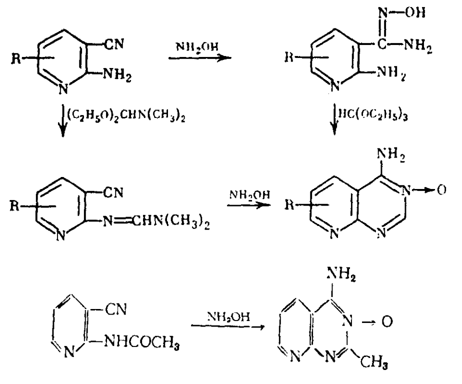


A pyridopyrimidine with an analogous structure has also been synthesised by condensing ethyl 4,4-dicyanobutyrate with guanidine.[93]

The reaction of 1-methyl-2-methylthiotetrahydropyridine with phenyl isothiocyanate afforded the corresponding thioamide, which cyclises on treatment with guanidine:[93]



The methods of synthesis of certain pyrido[2,3-d]pyrimidines, in particular the 3-*N*-oxides of 4-aminopyridopyrimidines, from 2-amino-3-cyanopyridines in accordance with the scheme[95,96]



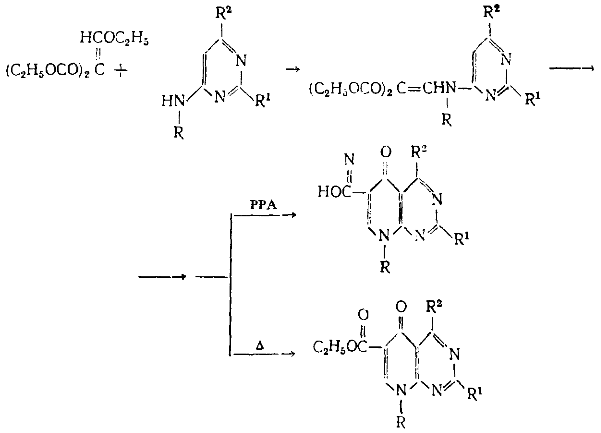
which have been described in the literature, are of interest.

The unsubstituted 5,6,7,8-tetrahydropyrido[2,3-d]pyrimidine has been obtained by condensing 2-piperidinone with formamide in the presence of phosphoryl chloride.[97,98]

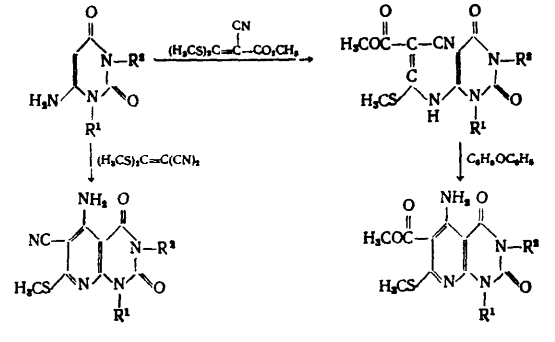
2. Synthesis from Pyrimidines

The methods described in this Section make it possible to obtain pyridopyrimidines with various substituents in the pyridine ring by forming the pyridine ring from pyrimidines with functional group substituents.

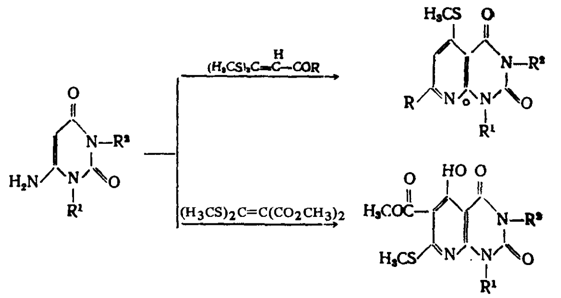
One of the commonest methods of synthesis of pyrido[2,3-*d*]pyrimidines involves the condensation of 4-aminopyrimidines with ethoxymethylenemalonic ester with subsequent cyclisation of the resulting compounds by treatment with phosphoryl chloride[99,100] or by refluxing in diphenyl ether.[101–105] Cyclisation in polyphosphoric acid (PPA) results in the formation of pyridopyrimidines with a carboxy-group in the pyridine ring:[106]



The reaction of 4-aminopyrimidines with cyanoethoxymethyleneacetic acid esters afforded the corresponding methyleneaminopyrimidines whose cyclisation is achieved in ethyl phosphate with subsequent hydrolysis by sodium hydroxide.[107] The condensation of 1,3-disubstituted 6-aminouracils with 2-cyano-3,3-bis(methylthio)acrylonitrile results in the formation in a single stage of 1,3-disubstituted 5-amino-6-cyano-7-methylthio-2,4-dioxo-1,2,3,4-tetrahydropyrido[2,3-d]pyrimidines. However, the reaction of the same 6-aminouracils with 2-cyano-3,3-bis(methylthio)acrylate under analogous conditions is accompanied by the formation of intermediates the heating of which in diphenyl ether also leads to the formation of pyridopyrimidines:[108]



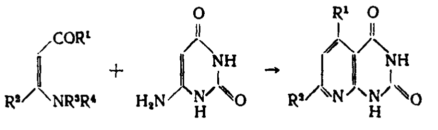
Other pyrido[2,3-d]pyrimidines containing various substituents in the pyridine ring were synthesised in the same study from 6-aminouracils in accordance with the scheme



New derivatives of pyridopyrimidines have been obtained by refluxing aminouracils with dimethyl acetylenedicarboxylate in protic solvents.[109,110]

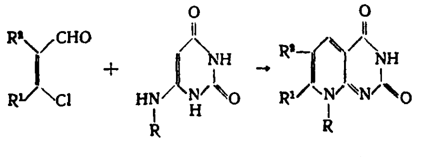
The reaction of 6-amino-1,3-dimethyluracil with unsaturated diketones also proceeds with formation of the pyridine ring.[111]

It has been shown that tetrahydropyrido[2,3-d]pyrimidines can be obtained in high yields by the reaction of 6-aminouracils with β-aminovinyl ketones:[112,113]

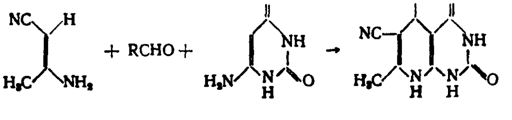


The cyclisation of 6-amino-1,3-dimethyluracil by reaction with unsaturated carbonyl compounds is carried out in the presence of basic or acid catalysts.[114]

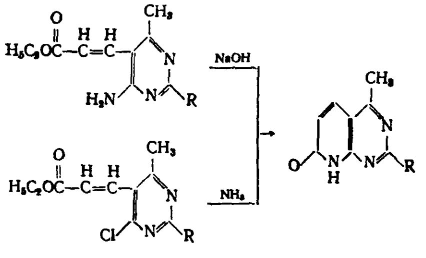
Heating of 6-aminouracils with β-chloro-substituted αβ-unsaturated carbonyl compounds in DMF leads to the formation of 6,7,8-trisubstituted pyridopyrimidines:[115]



A novel method of synthesis of certain pyridopyrimidine derivatives involves the interaction of 6-aminouracils with bisacetonitrile and aldehydes:[116]

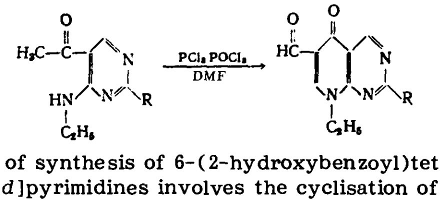


Methods of synthesis of 2-substituted 4-methyl-7-oxopyridopyrimidines based on the reaction of 2-substituted 4-amino-5-iodo-6-methyl- and 5-iodo-6-methyl-4-oxo-pyrimidines with ethyl acrylate in accordance with the scheme

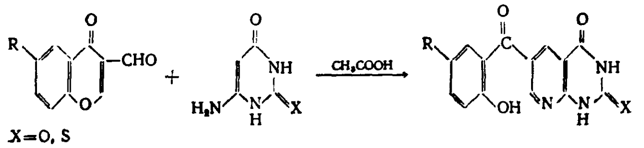


have been described.[117] Derivatives of 7-oxopyridopyrimidines can also be obtained by condensing 6-aminouracils with ethyl acrylate.[118]

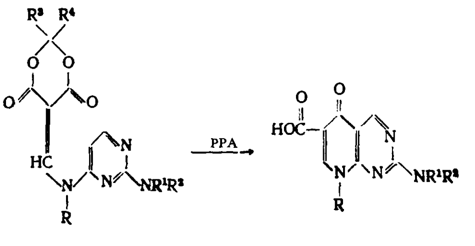
6-Formylpyridopyrimidines have been synthesised by the reaction of 2,4-diaminopyridines with DMF in the presence of phosphorus trichloride or phosphoryl chloride.[119] Other derivatives of 6-formylpyrido[2,3-*d*]pyrimidines have been synthesised under analogous conditions from 5-acetyl-4-ethylaminopyrimidines:[120,121]



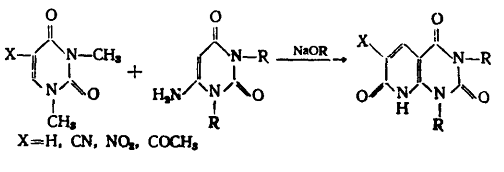
A method of synthesis of 6-(2-hydroxybenzoyl)tetrahydropyrido[2,3-*d*]pyrimidines involves the cyclisation of 4-aminouracils by reaction with chromene derivatives in acetic acid:[122]



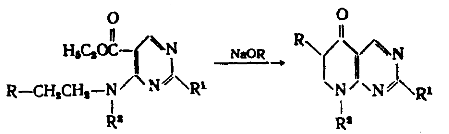
A new method of synthesising derivatives of 6-carboxypyridopyrimidines via the scheme[123–125]



has been developed. A single-stage synthesis of pyridopyrimidines from two molecules of substituted uracils has been proposed:[126,127]

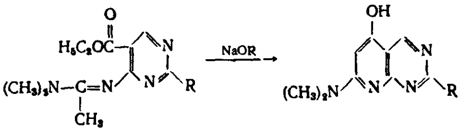


4-(2-Cyanoethyl)- or 4-(2-ethoxycarbonylethyl)-amino-5-ethoxycarbonyl pyrimidines, obtained by the reaction of 4-chloro-5-ethoxycarbonylpyrimidines with the nitriles or esters of 3-aminopropionic acids, cyclise on treatment with sodium alkoxides or hydride with formation of the corresponding 5-oxo-5,6,7,8-tetrahydropyrido[2,3-*d*]pyrimidines:[128–141]



When 4-amino-5-ethoxycarbonylpyrimidines are acylated with the chloride of the monoethyl ester of malonic acid in the presence of alkoxide, intramolecular cyclisation takes place with formation of 5,7-dioxo-5,6,7,8-tetrahydropyridopyrimidines.[142–144]

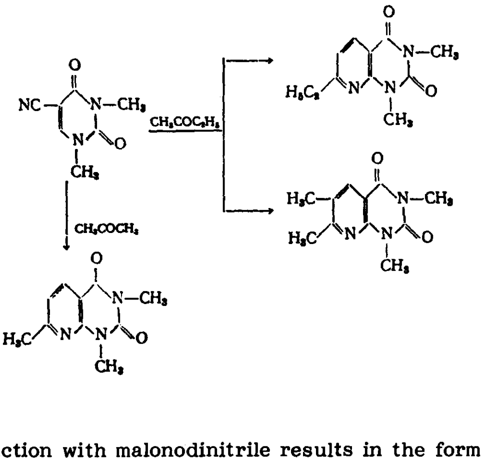
The amines formed as a result of the condensation of 4-amino-5-ethoxycarbonylpyrimidines with the diethyl acetal of dimethylacetamide in the presence of sodium alkoxide cyclise to 5-hydroxypyridopyrimidines:[145,146]



The condensation of 4-amino-5-methoxycarbonylpyrimidines with butenal, which led to the synthesis of *N*-substituted 5-oxo-6-vinyl-5,6-dihydropyridopyrimidine, has also been investigated.[147]

The reaction of 4-aminopyrimidines containing the formyl group in the 5-position with aryl acetonitriles, ketones, and cyanoacetamides yields the corresponding pyrido[2,3-*d*]-pyrimidines.[148–153]

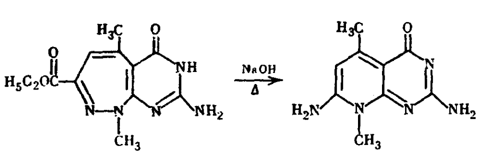
The condensation of 5-cyano-1,3-dimethyluracil with acetone involves the closure of the pyridine ring with formation of the trimethyl derivative, while treatement with butanone under the same conditions yields a mixture of the two isomeric dioxotetrahydropyrido[2,3-d]pyramidines:[154]



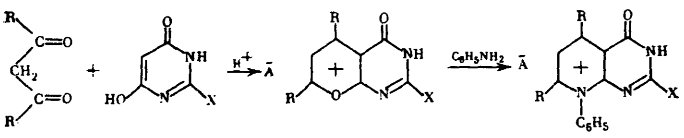
The reaction with malonodinitrile results in the formation of 7-amino-6-cyanodioxotetrahydropyrido[2,3-*d*]pyrimidine.[154]

Various derivatives of 2-thionopyridopyrimidines have been obtained by condensing arylidenethiobarbituric acid with malonodinitrile, ethyl cyanoacetate, and ethyl acetoacetate in the presence of ammonium acetate.[155]

An interesting condensation of 2-amino-4-(1-*N*-methylhydrazino)pyrimidine with ethyl 3-acetylpyruvate takes place with formation of 8-amino-3-ethoxycarbonyl-1,5-dimethyl-6-oxo-6,7-dihydropyrimido[4,5-*c*]-1,2-diazepine, whose treatment with potassium hydroxide leads to 2,7-diamino-5,8-dimethyl-4-oxo-4,8-dihydropyrido[2,3-d]pyrimidine:[156]



The synthesis of 8-phenylpyrido[2,3-*d*]pyrimidinium salts from 4,6-dihydroxypyrimidines and diketones via salts of pyrylio[2,3-*d*]pyrimidines in accordance with the following scheme has been reported:[158]



X = OH. SH. NH_2. SCH_3: A = ClO_4. H_2PO_4. CF_3COO

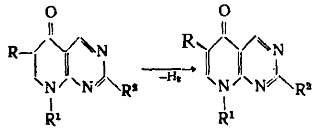
Treatment of pyrano[2,3-d]pyrimidine with aqueous ammonia solution leads to the replacement of the pyran ring by the pyridine ring, which results in the formation of 2,4-dioxopyridopyrimidine.[158]

III. CHEMICAL REACTIONS

The chemical reactions of condensed pyridopyrimidines can be carried out selectively, via the pyridine or pyrimidine ring, which makes it possible to obtain a large number of new derivatives of this series. The chemical reactions of pyridopyrimidines involving the opening of the pyrimidine ring have also been studied.

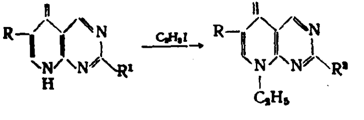
1. Reactions Via the Pyridine Component of the Molecule

It has been shown that 2,8-disubstituted 6-alkoxycarbonyl-5-oxo- or 6-cyano-5-oxo-tetrahydropyrido[2,3-*d*]pyrimidines are dehydrogenated on treatment with various dehydrogenating agents:[132,159–163]



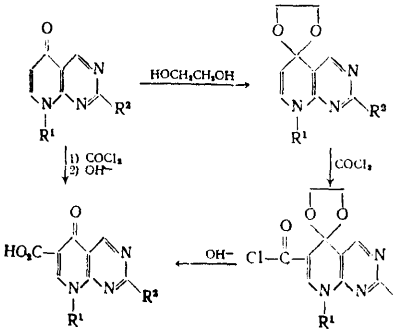
An analogous result has been obtained on brominating 2,8-disubstituted 5-oxotetrahydropyridopyrimidines with subsequent dehydrobromination of the products.[131,133,137]

5-Oxopyridopyrimidines are readily alkylated with ethyl iodide to form the corresponding 8-ethyl derivatives:[102–104,164,165]



Various methods of synthesis of derivatives of condensed pyridopyrimidines containing the carboxy-group in the 6-position have been developed.[102–104,132,133,166–174] Thus it has been shown that the hydrolysis of 6-ethoxycarbonylpyridopyrimidines leads to 6-carboxypyridopyrimidines in high yields.[102–104,132,133,166] 6-Formyl and 6-acyl derivatives of pyridopyrimidines are oxidised on treatment with various oxidants to the corresponding carboxypyridopyrimidines.[167,169] Heating of 6-oxazolidinylpyridopyrimidines in hydrochloric acid leads to the same result.[170]

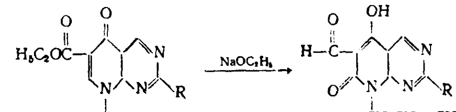
6-Carboxy-derivatives have been obtained in one or three stages from 8-alkyl-5-oxo-5,8-dihydropyridopyrimidines and phosgene:[171–173]



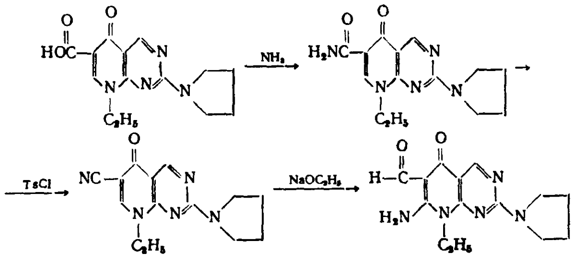
5-Alkylamino-6-carboxypyrido[2,3-d]pyrimidines can be obtained by hydrolysing 6-alkoxycarbonyl-5-alkylaminopyridopyrimidines.[174] Other workers established[147] that the oxidation of 6-vinylpyridopyrimidine with potassium permanganate leads to its 6-carboxy-derivative.

The alkylation of 8-alkyl-6-cyano- or 6-alkoxycarbonyl-8-alkyl-5-oxopyridopyrimidines has been investigated and it has been shown that the alkyl group enters the 6-position in the presence of sodium alkoxide.[132,136]

In the presence of sodium alkoxide, derivatives of 6-ethoxycarbonyl-5-oxo-5,8-dihydropyridopyrimidines are converted into the corresponding 6-formyl-5-hydroxy-7-oxopyrido[2,3-d]pyrimidines:[175]



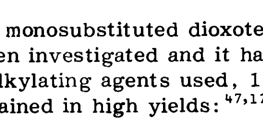
In the sams study the authors proposed the synthesis of 7-amino-8-ethyl-6-formyl-5-oxo-2-(1-pyrrolidino)-5,8-dihydropyrido[2,3-d]pyrimidine from 6-carboxypyridopyrimidine:



The oxo-group is substituted by chlorine atome when 5-oxopyridopyrimidines are treated with phosphoryl chloride. The subsequent interaction of 5-chloropyridopyrimidines with alcohols and amines leads to 5-alkoxy- and 5-amino-derivatives.[146]

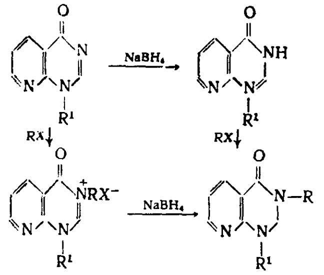
2. Reactions Via the Pyrimidine Component of the Molecule

The alkylation of monosubstituted dioxotetrahydropyridopyrimidines has been investigated and it has been shown that, regardless of the alkylating agents used, 1,3-disubstituted derivatives are obtained in high yields:[47,176–181]



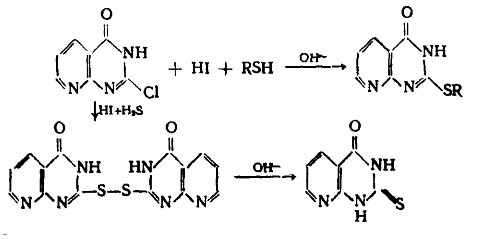
The alkylation of 1-substituted 2-oxo-1,2,3,4-tetrahydropyrido[2,3-d]pyrimidines also takes place readily.[182–184]

The interaction of 1-substituted 4-oxo-1,4-dihydropyridopyrimidines with alkyl halides and dialkyl sulphates results in the formation of the corresponding salts of the 3-*N*-alkyl derivatives, whose treatment with sodium tetrahydroborate is accompanied by the reduction of the C=N double bond in the pyrimidine ring.[185] The same workers[186] proposed another method for the 3-*N*-alkylation of pyridopyrimidines, which involves essentially the initial reduction of the C=N double bond in the initial pyridopyrimidines with subsequent alkylation of the products:

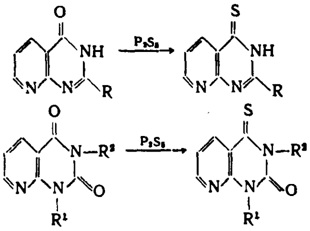


One of the important reactions of 2-oxo-, 4-oxo-, and 2,4-dioxo-pyrido pyrimidines is their conversion by treatment with phosphoryl chloride into the 2-chloro-, 4-chloro-, and 2,4-dichloro-derivatives—the starting materials for the synthesis of many pyridopyrimidine derivatives by the nucleophilic substitution of the chlorine atom. Thus the interaction of chloropyridopyrimidines with alcohols, amines, and ketones yielded the corresponding alkoxy-, amino-, and oxomethyl derivatives.[32,187–192]

The interaction of 2-chloro-4-oxodihydropyridopyrimidine with alkanethiols in the presence of hydrogen iodide afforded the corresponding 2-alkylthio-derivatives, while the reaction with hydrogen sulphide under the same conditions leads to the formation of the disulphide, which is converted into the 2-thiono-derivative as a result of hydrolysis:[193]

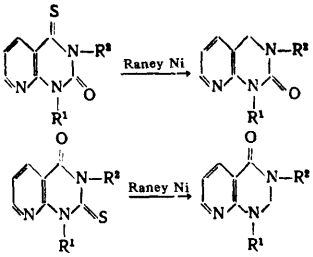


4-Oxodihydro- and 2,4-dioxotetrahydro-pyridopyrimidines are converted into the corresponding 4-thionopyridopyrimidines in high yields on treatment with phosphorus pentasulphide:[187,194]



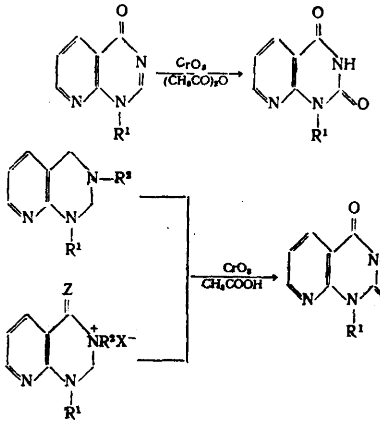
The conversion of thionopyridopyrimidines into oxopyridopyrimidines by oxidising the thiono-group with hydrogen peroxide is also possible.[195–197]

Thionopyridopyrimidines are desulphurised in the presence of Raney nickel as catalyst:[198,199]

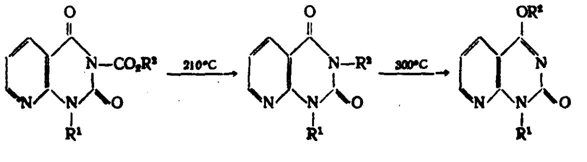


It has been shown that, on treatment with a 5% solution of sodium hydroxide, 2,4-diaminopyrido[2,3-d]pyrimidine is converted into 4-amino-2-oxo-1,2-dihydropyridopyrimidine.[91]

2,4-Dioxopyridopyrimidines are obtained by oxidising various pyridopyrimidine derivatives with chromium trioxide:[200–202]

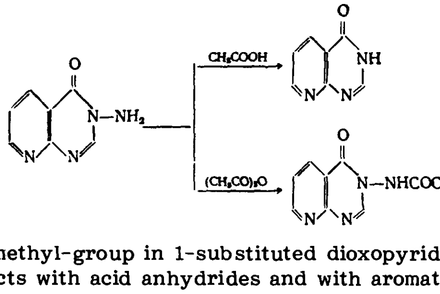


A study of the decarboxylation of 3-alkoxycarbonyl-2,4-dioxotetrahydropyridopyrimidines showed that different products are obtained depending on the temperature. Thus the corresponding 3-alkyl derivatives are formed at 210 °C, while on raising the temperature to 300 °C the alkyl group migrates from the nitrogen atom in the 3-position in the pyrimidine ring to the oxygen atom in the 4-position:[203,204]



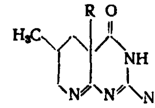
6-Substituted 8-ethyl-5-oxo-5,8-dihydropyrido[2,3-d]pyrimidines, containing the 2-methylthio-, 2-methylsulphoxy-, and 2-chloro-substituents, undergo substitution reactions with amines, forming the corresponding amino-derivatives.[101,121,205–210]

It has been shown that the interaction of 3-amino-4-oxo-3,4-dihydropyridopyrimidine with pentyl nitrite in the presence of acetic acid entails its deamination, while in the reaction with acetic anhydride the amino-group is acylated:[36]



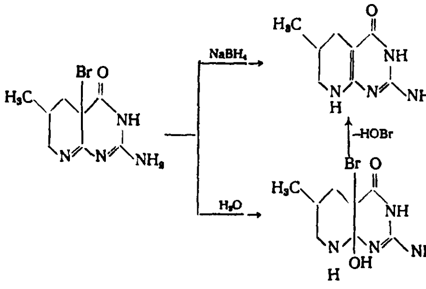
The 2-methyl-group in 1-substituted dioxopyridopyrimidines reacts with acid anhydrides and with aromatic aldehydes to form the corresponding 2-acylmethyl and 2-styryl derivatives.[211–213]

Various chemical reactions of 2-amino-6-methyl-4-oxohexahydropyridopyrimidine, in particular those making it possible to obtain new derivatives with angular substituents, have been investigated:[214,215]

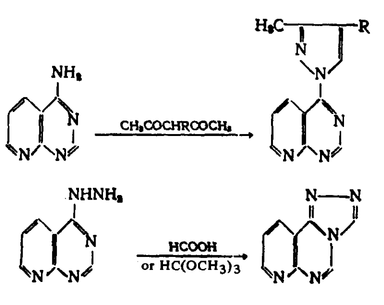


R=HOO, OH, Br

Hexhydropyridopyrimidine containing an angular bromine atom is converted by treatment with sodium tetrahydroborate into the initial pyridopyrimidine, while treatment with water entails an addition reaction which results in the formation of octahydropyridopyrimidine with two angular substituents (OH and Br), which readily splits off hypobromous acid:[215]



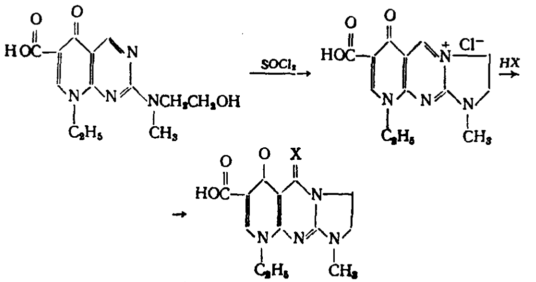
The reactions of substituted pyridopyrimidines via the substituents in the pyrimidine ring, which lead to the formation of tricyclic systems, are of great interest. Thus the condensation of 4-aminopyridopyrimidine with β-diketones and of 4-hydrazinopyridopyrimidine with formic acid or its orthoester afforded the corresponding 1-(4-pyrazolyl)pyridopyrimidine and triazolo[3,4-*f*]pyridopyrimidine:[216]



1-Subsituted 5-oxo[*H*]triazole[3,4-*f*]pyridopyrimidines have been obtained by an analogous procedure.[217]

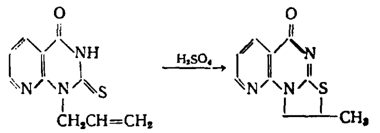
The interaction of 2-amino-3-(5-tetrazolyl)pyridine with orthoesters leads to a condensed tricyclic system—pyrido[2,3-d]tetrazolo[5,1-*f*]pyrimidine.[218,219]

Imidazopyridopyrimidine has been synthesised by the reaction of 2-(β-hydroxyethylamino)pyridopyrimidine with thionyl chloride:[220]

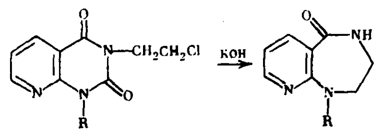


$X=OH, OCH_3, OC_2H_5, CH_2COCH_3$

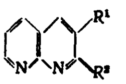
1-Allyl-4-oxo-2-thiono-1,2,3,4-tetrahydropyrido[2,3-*d*]pyrimidine undergoes intramolecular cyclisation in the presence of concentrated sulphuric acid with formation of the condensed thiazolidinopyridopyrimidine:[85]



One of the interesting reactions of 1-substituted 3-(β-chloroethyl)-2,4-dioxotetrahydropyridopyrimidines is their conversion into derivatives of pyrido-1,4-diazepines by treatment with an alcoholic solution of potassium hydroxide:[221]



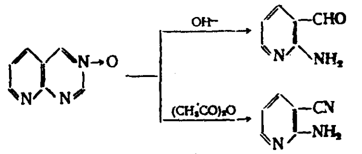
A number of reactions of pyridopyrimidine 3-oxide derivatives with ethyl cyanoacetate, ethyl acetoacetate, and malonodinitrile, leading to the corresponding 1,8-naphthyridines, have been carried out:[222]



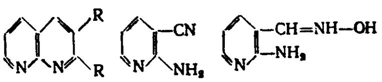
$R^1=CO_2C_2H_5, R^2=NH_2; R^1=CN, R^2=NH_2; R^1=CO_2C_2H_5, R^2=CH_3$

3. Reactions Involving the Opening of the Pyridine Ring

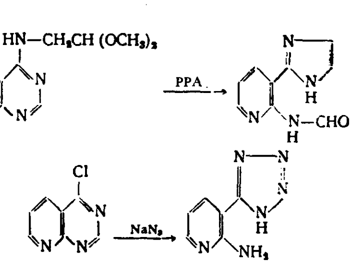
The pyramidine ring in pyrido[2,3-d]pyrimidines is known to be opened in the presence of both bases and acids. 2-Amino-3-carboxypyridines are obtained in the former case[87,223] and the 2-amino-3-formyl derivatives are formed in the latter case.[151] Treatment of 3-hydroxypyridopyrimidine with sodium or potassium hydroxide also leads to an aminoformylpyridine.[222] The opening of the pyrimidine ring by treatment with acetic anhydride has been described in the same study:



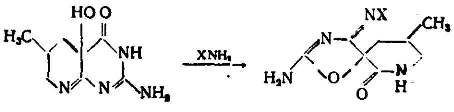
The condensation of 3-hydroxypyridopyrimidine with ketones has also been investigated and it has been established that a mixture of three compounds with the following structures is formed:[224]



The opening of the pyrimidine ring has been studied in the dimethyl acetal of 4-pyridopyrimidinylaminoacetaldehyde and 4-chloropyridopyrimidine when the latter are treated with polyphosphoric acid (PPA) and sodium azide respectively:[218,219]

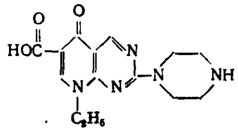


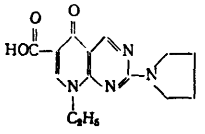
The condensation of the 2-amino-10-hydroxy-4-oxo-derivatives with methoxyamine and semicarbazide, which results in the formation of spiro-oxazolopiperidine derivatives, is also of interest:[215]



IV. BIOLOGICAL PROPERTIES

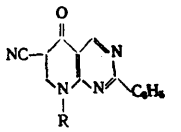
As mentioned above, derivatives belonging to the class of pyrido[2,3-d]pyrimidines exhibit a broad spectrum of biological activity, two representatives being used as effective antibacterial agents in medical practice under the names "pipemidic acid"[5,225–244] and "piromidic acid".[6,245–254]



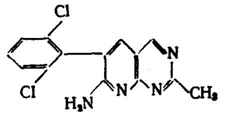


The study of the antibacterial activity of analogous derivatives containing various substituents in the 2-, 6-, and 8-positions showed that, for identical substituents in the 2- and 8-positions, the highest activity is shown by compounds with a carboxy-group in the 6-position. The most effective compounds are pyridopyrimidines with ethyl and amino-groups in the 2- and 8-positions respectively.[100,103,104,133–138,160,164,166,174,203,255–260] Furthermore, certain derivatives of this series exhibit anti-inflammatory analgesic,[206,261] and hypotensive[149,205] activities.

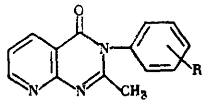
8-Substituted 6-cyano-5-oxo-2-phenyl-5,6,7,8-tetrahydropyridopyrimidines[128–130] exert a depressing activity on the central nervous system.



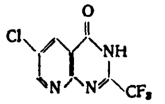
An effective hypotensive agent has been found among 2-substituted 7-amino-6-aryl derivatives:[3,149,150]



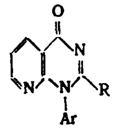
2-Substituted 4-oxodihydropyrido[2,3-d]pyrimidines exhibit antiallergic[25,29,262] and diuretic[26–28,30,263–265] activities. 3-Aryl-2-methyl-4-oxodihydropyridopyrimidines containing different substituents in the benzene ring are effective inhibitors of xanthine oxidase:[4]



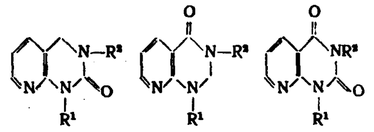
Among derivatives of 2-alkyl(or halogenoalkyl)-4-oxo-3,4-dihydropyridopyrimidines, containing various substituents in the pyridine ring, the 6-chloro-2-trifluoromethyl derivative with a strong herbicidal activity has been discovered:[2]



1-Aryl-4-oxotetrahydropyridopyrimidines exhibit diuretic, hypotensive anti-inflammatory, and tranquillising activities.[19–21] 2-Substituted derivatives of this series are also analgesics and depressants:[23,24,211,212]

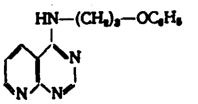


Almost all 2-oxo-derivatives,[12,13,182–184,209] 4-oxo-derivatives,[185,186,195,210,266] and 2,4-dioxo-derivatives[41,51,54–58,60–66,176–181,196–201] of 1,3-disubstituted tetrahydropyrido[2,3-d]pyrimidines show analgesic and anti-inflammatory activities and are depressants:



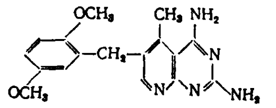
4-Oxo-2-thiono- and 2-oxo-4-thiono-tetrahydropyridopyrimidines possess the same properties[79–82,194] and some of them exhibit antihistamine[76] and diuretic[192] activities.

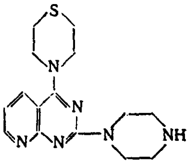
Whereas 4-chloropyridopyrimidines are neuroleptic substances,[187] the 4-alkoxy(or 4-amino)-derivatives are spasmolytic substances.[32,188] This series also includes a powerful antifungal agent—4-(3-phenoxypropylamino)pyrido[2,3-d]pyrimidine:[267]



The series of 1-substituted 4,7-diaminopyridopyrimidines includes effective depressants of the central nervous system.[152,153]

Among derivatives of 2,4-diaminopyridopyrimidines, it is possible to distinguish two compounds: the first is an effective inhibitor of several enzymes[1] and the second inhibits the aggregation of thrombocytes:[268]





Antibacterial properties have been found in certain derivatives of pyridopyrimidines containing the penicillanic acid residue.[269,270]

In conclusion it should be stated that a more far-reaching study of the methods of synthesis and new derivatives of pyrido[2,3-d]pyrimidines, directed towards the development of other methods or the simplification of individual stages of existing methods of synthesis, is of great theoretical and practical interest for the preparation of new, hitherto unknown, biologically active compounds and medicinal preparations.

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Radical Polymerisation in the Associated Species of Ionogenic Surface-active Monomers in Water

V.V.Egorov and V.P.Zubov

The radical polymerisation in water of ionogenic monomers of the cationic and anionic type exhibiting surface-active properties is discussed. Together with kinetic phenomena, which can be accounted for within the framework of the hypothesis of a homophase course of the process, effects which require the assumption of the possibility of the association of the monomeric molecules are observed in the polymerisation of monomers with a low surface activity in aqueous solutions. The polymerisation of monomers with a high surface activity in micellar dispersions differs from the processes in solutions by a number of features associated with the influence of structure formation in the monomer on the kinetics of polymerisation and the macrostructure of the polymer formed. The kinetic effects induced by the increasing concentration and microviscosity of the monomer solutions and also by the change in the relative positions of its molecules in the associated species compared with the solution are discussed. Examples of the influence of processes involving the rearrangement of the associated speices on the process kinetics are presented. The possibility, in principle, of the fixation of the structure of the associated species (micelles) as a consequence of polymerisation is noted.

The kinetics of the polymerisation process in micellar and vesicular dispersions of two-chain surface-active monomers and also in monolayers at the water-gas interface are discussed.

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I. INTRODUCTION

The branch of polymer chemistry associated with the synthesis of surface-active monomers and the study of the characteristic features of their polymerisation in various media has developed widely during the last decade. The application of these compounds makes it possible to investigate the influence of processes involving the association of monomeric molecules on the kinetics of radical polymerisation in solution. Here one may expect, on the one hand, the appearance of kinetic effects associated with the formation of micelles in aqueous dispersions of surface-active monomers (SAM) (concentration effect associated with the appearance of an interface and others), which are known for a number of organic reactions in such systems.[1-4] On the other hand, there appears a possibility of studying the role of the mutual orientation of the molecules or their fragments in chemical reactions and hence of modelling certain enzymic processes.[5-7]

It is known from the literature that the kinetics of polymerisation in solution is influenced by processes involving the association of monomeric molecules induced by hydrophobic,[8] electrostatic,[9] and $\pi-\pi$ interactions[10] as well as association processes via the formation of hydrogen bonds between molecules.[11] The manifestation of effects of this kind is to be expected also in micellar SAM solutions. Organic solutions of ionogenic monomers, in which association phenomena have also been observed,[12-14] are not considered in this review. Attention will be concentrated on micellar and vesicular SAM dispersions in water and also on monolayers of monomers at the water–gas interface.

The practical importance of surface-active monomers is associated with the synthesis of the corresponding polyelectrolytes (via homo- and co-polymerisation) which have found applications in various branches of science and engineering as sorbents, flocculants, emulsion stabilisers etc.[15] One of the newest and most promising developments is the creation on their bases of carriers for the immobilisation of biological and medical preparations.[16,17] Emulsion polymerisation using SAM as copolymerising emulsifying agents is of independent importance.[18,19]

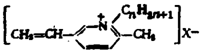
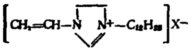
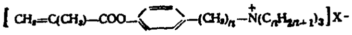
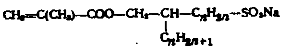
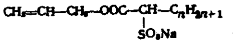
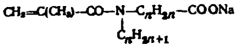
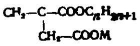
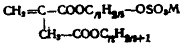
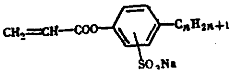
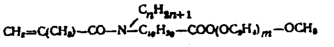
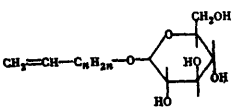
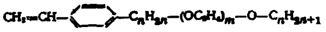
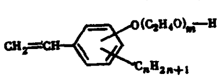
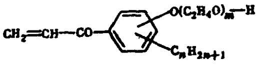
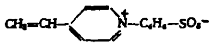
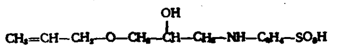
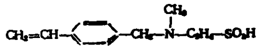
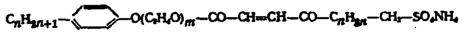
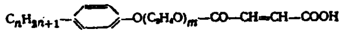
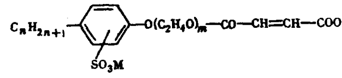
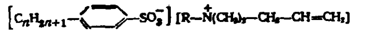
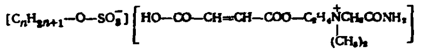
II. CLASSIFICATION OF SURFACE–ACTIVE MONOMERS

Table 1 presents the principal classes of SAM and indicates their typical representatives. It follows from the table that the number of SAM known at the present time is fairly large. Individual SAM differ by the nature of the hydrophilic component, the so called "head" (anionic, cationic, non-ionic, mixed, and complex), the activity of the polymerising group (vinyl, allyl, acrylic, styrene, maleic, etc.), and also the length of the aliphatic chain—the "tail".

In water, the above compounds, which are typical organic surfactants, are capable of forming both true and micellar solutions.[70] Furthermore, monomers which are structural analogues of phospholipids, containing in the molecule two extended aliphatic chains, are able to form structures resembling biological membranes in solution (vesicles, liposomes)[16] and at the interface (monolayers and polylayers[16]).

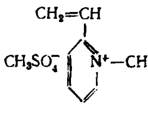
Yet another type of structural organisation of SAM is associated with the preparation in their presence of stable direct and inverted emulsions of compounds which are sparingly soluble respectively in water or oil, in particular vinyl monomers.[19] However, in such systems the SAM association effects have not been observed in an explicit form. Therefore, despite the enormous industrial importance of the emulsion polymerisation process in the presence of copolymerising emulsifying agents,[19] it is not considered in this review.

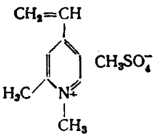
Table 1. Surface-active monomers ($X = Cl^-$, Br^-, I^-, or $CH_3SO_4^-$ anion; $M = Na^+$, K^+, or NH_4^+ cation).

Monomer	Refs.
Cationic type	
	[20, 21]
$[(CH_2{=}CH{-}CH_2)_m\overset{+}{N}(CH_3)_{3-m}{-}C_nH_{2n+1}]X^-$	[22–26]
$[CH_2{=}C(CH_3){-}COO{-}R'{-}\overset{+}{N}(CH_3)_2{-}C_nH_{2n+1}]X^-$	[27]
	[28 29]
	[30]
	[31]
$[CH_2{=}CH{-}CH_2{-}O{-}CO{-}CH_2\overset{+}{N}(CH_3)_2{-}C_nH_{2n+1}]Cl^-$	[32]
$[CH_2{=}CH{-}O{-}C_2H_4{-}\overset{+}{N}(CH_3)_2{-}C_nH_{2n+1}]Cl^-$	[33]
Anionic type	
 $CH_2{=}C(CH_3){-}COO{-}CH_2{-}\underset{C_nH_{2n+1}}{\underset{\vert}{CH}}{-}C_nH_{2n}{-}SO_3Na$	[34, 35]
$CH_2{=}CH{-}OSO_3Na$	[36]
 $CH_2{=}CH{-}CH_2{-}OOC{-}\underset{SO_3Na}{\underset{\vert}{CH}}{-}C_nH_{2n+1}$	[37]
 $CH_2{=}C(CH_3){-}CO{-}\underset{C_nH_{2n+1}}{\underset{\vert}{N}}{-}C_nH_{2n}{-}COONa$	[38]
	[30]
$C_nH_{2n+1}{-}CH{\equiv}CH{-}CH{\equiv}CH{-}C_nH_{2n}{-}COOM$	[39, 40]
$CH_2{=}CH{-}C_nH_{2n}{-}COONa$	[41]
$C_nH_{2n+1}{-}OOC{-}CH{=}CH{-}COOM$	[42, 43]
$C_nH_{2n+1}{-}OOC{-}CH{=}CH{-}COO{-}C_nH_{2n}{-}SO_3M$	[44, 49]
$C_nH_{2n+1}{-}NH{-}OC{-}CH{=}CH{-}COO{-}C_nH_{2n}{-}OSO_3M$	[49]
 $CH_2{-}\underset{CH_2{-}COOM}{\underset{\vert}{C}}{-}COOC_nH_{2n+1}$	[50]
 $CH_2{=}\underset{CH_2{-}COOC_nH_{2n+1}}{\underset{\vert}{C}}{-}COOC_nH_{2n}{-}OSO_3M$	[51]
	[52]
	[53]
Non-ionic type	
 $CH_2{=}C(CH_3){-}CO{-}\overset{C_nH_{2n+1}}{N}{-}C_{10}H_{20}{-}COO(OC_2H_4)_m{-}OCH_3$	[38]
$CH_2{=}C(CH_3){-}COO{-}C_nH_{2n}{-}O(C_2H_4O)_m{-}H$	[30, 54]
$CH_2{=}C(CH_3){-}COO{-}C_nH_{2n+1}$	[53]
Mixed type	
	[56, 57]
$CH_2{=}CH{-}CH_2{-}O(C_2H_4O)_m{-}C_nH_{2n+1}$	[58, 59]
$CH_2{=}C(CH_3){-}COO{-}(C_2H_4O)_m{-}(C_3H_6O)_n{-}H$	[60]
	[61]
$CH_2{=}CH{-}COO{-}(C_2H_4O)_m{-}C_nH_{2n+1}$	[61, 62]
	[61]
	[61]
$[H{-}O{-}CO{-}CH{=}CH{-}COO{-}CH_2{-}CH_2{-}\overset{+}{N}(CH_3)_2{-}C_nH_{2n+1}]Cl^-$	[33]
	[63]
 $CH_2{=}CH{-}CH_2{-}O{-}CH_2{-}\overset{OH}{\overset{\vert}{C}}H{-}CH_2{-}NH{-}C_2H_4{-}SO_3H$	[64]
	[64]
	[51]
	[65]
	[66]
$C_nH_{2n+1}{-}O{-}(C_2H_4O)_m{-}CO{-}CH{=}CH{-}COO{-}C_2H_4{-}SO_3Na$	[67]
Complex type	
	[68]
 $[C_nH_{2n+1}{-}O{-}SO_3^-]\left[HO{-}CO{-}CH{=}CH{-}COO{-}C_2H_4\underset{(CH_3)_2}{\underset{\vert}{\overset{+}{N}}}CH_2CONH_2\right]$	[69]

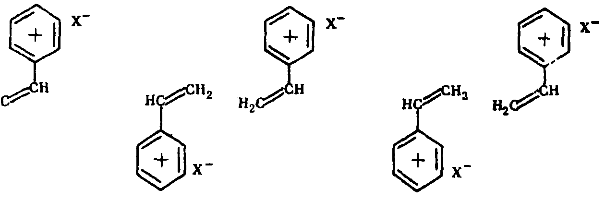
III. POLYMERISATION IN SOLUTIONS OF MONOMERS HAVING A LOW SURFACE ACTIVITY

The phenomenon of the organisation of monomeric molecules in solution has been observed for ionogenic monomers without pronounced surface-active properties. The spontaneous (in the absence of material initiators and other sources of free radicals, ions, etc.) polymerisation of vinylpyridine salts in solutions has been investigated.[20,21,70–74] Fig.1*a* presents the dependence of the initial rate of the spontaneous polymerisation of compounds based on 2-vinylpyridine or 2-methyl-5-vinylpyridine and dimethyl sulphate on the concentration of the monomers in water:[71]

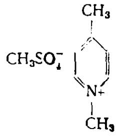

(I)


(II)

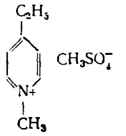
Contrary to expectation, the rate of the process in the given system increases non-linearly with the monomer concentration, which is a consequence, according to the authors, of the formation from the monomer molecules of associated species with the following structure



This hypothesis makes it possible to explain the extremum in the temperature dependence of the rate of polymerisation of the above monomers (Fig.1*b*): the usual increase of the rate of the process with increasing temperature should be accompanied in this case by an increase in the contribution by the competing process involving the decomposition of the associated species and the consequent decrease in the rate of polymerisation. The hypothesis of the association of the monomeric molecules has been confirmed[78] by the character of the dependence of the viscosity of the solutions of pyridinium salts on their concentration in water (Fig.2):



(III)



(IV)

Above a certain concentration, the slope of the straight line increases and it is known[22] that this may be associated with the appearance of associated surfactants species in solution.

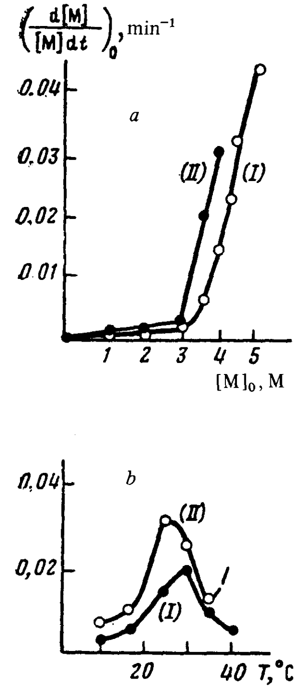


Figure 1. Dependence of the reduced initial rate of polymerisation of the vinylpyridinium monomers (I) and (II) in water on their initial concentration at 50 °C (*a*) and on temperature at [M] = 4 M (*b*).[71]

The influence of the association of the monomers on the kinetics and mechanism of the spontaneous polymerisation has been demonstrated in relation to acid vinylpyridinium salts, which are capable of forming micelles in water above a certain concentration (CCM).[72-74] Fig.3 illustrates the dependence of the critical concentration for the formation of micelles from a monomer based on 4-vinylpyridine and perchloric acid on the concentration of inert electrolyte in solution.[74] In the course of the spontaneous polymerisation over the entire range of monomer concentrations (at a fixed electrolyte concentration) below the CCM, the formation of ionene via a polyaddition mechanism is observed,[73] while above the CCM the 1,2-polymer is formed. A more detailed study of the formation reactions of these products showed[27] that both reactions take place over the entire range of monomer concentrations and that a plot, in terms of double logarithmic coordinates, of the rate of the process against the monomer concentration for each reaction considered separately does not exhibit a break. According to the authors,[27] this indicates the absence of the influence of monomer association on the polymerisation kinetics in the given system. However, the entire set of data, including the data of the above authors,[27] shows that the associated form of the monomer undergoes preferential polymerisation of the kind known for concentrated solutions of vinylpyridinium salts,[75] whereas in dilute solutions polyaddition takes place.[28,29] It is also essential to take into account the authors' view[27,28] that, in the analysis of the reactions of the monomers indicated in concentrated solutions, it is necessary to include not only the effect of association but also the influence of the ionic strength of the solution on the degree of dissociation of the monomeric salt and hence on its behaviour in the homopolymerisation reaction.

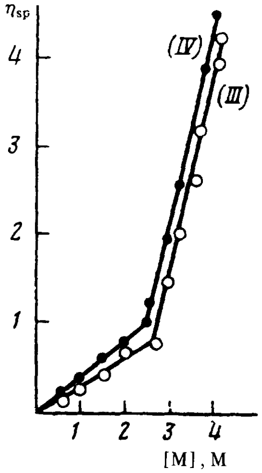


Figure 2. Concentration dependence of the specific viscosity of aqueous solutions of the pyridinium salts (III) and (IV) at 25 °C.[78]

Another type of cationic monomer—allylammonium salts—has been investigated.[22,23,76,77] The study of the kinetics of the radical polymerisation of dimethylallylammonium chloride in water yielded high reactions orders with respect to the monomer (2.9) and the initiator (0.8).[23] The rate of the process and the viscosity of the solution increased non-linearly with increase in the monomer concentration. The addition of an inert electrolyte increased the rate of the reaction and reduced its order with respect to the monomer. The observed effects are a consequence, according to the authors,[23] of the electrostatic interactions of the reaction components in solution and they are associated primarily with the influence on the overall process rate of the changes in the constants for chain initiation and propagation as a function of the monomer concentration. However, the data of Topchiev and Nazhmetdinova[76] show that the change in the termination rate constant k_t also plays a significant role. The fact that the dependence of the rate of polymerisation V_p on the monomer concentration [M] can be expressed by a linear plot of lg V_p against lg $[M]\eta_{rel}^{0.5}$, where η_{rel} is the relative viscosity of the solution, indicates unambiguously, according to the above investigators,[76] the decisive influence of viscosity on the chain termination rate constant and hence on the overall rate of the process. At the same time, the non-linearity of the dependence of the viscosity of aqueous solutions of the monomers on the concentration of the monomer salt[23] is striking, which may be a consequence of the association of the monomeric molecules.[22] However, this finding is not discussed by Wandrey et al.[23]

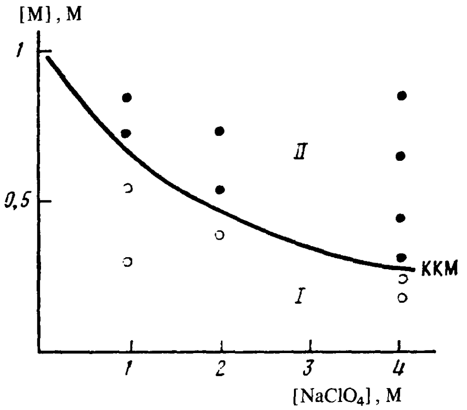


Figure 3. Dependence of the critical concentration for micelle formation of the salt of 4-vinylpyridine and perchloric acid on the sodium perchlorate concentration in water at 20 °C:[74] I) region corresponding to the formation of polyionene; II) region corresponding to the formation of the 1,2-polymer in the polymerisation of 4-vinylpyridinium perchlorate at a fixed electrolyte concentration; the circles correspond to the monomer and electrolyte concentrations used.

A high order of the reaction has been observed also in the study of the spontaneous (radical) polymerisation of the hydrochloride of *NN*-diethylaminoethyl methacrylate in water.[78] It was found that at 60 °C, below a certain critical concentration of the monomer (2–2.5 M), the rate of reaction increases in proportion to the monomer concentration raised to the power of 1.2 and that above this concentration it increases in proportion to the concentration raised to the power of 4.7. Under these conditions, the increase in the concentration of the monomer salt is accompanied by a decrease in the viscosity of the polymer formed, which is associated, according to the authors,[78] with the occurrence of chain transfer to the monomer. When the process temperature is reduced to 20 °C, the dependence of the initial rate of polymerisation on the monomer concentration passes through a maximum. The increase in the rate of the process with increasing concentration along the initial section of the relation has been explained[78] by the appearance of aggregates of the monomeric molecules in the system.

An extremum in the dependence of the rate of radical polymerisation on the monomer concentration in water has also been observed for an anionic monomer–sodium ethylenesulphonate.[36] The increase in the rate of the process may be caused by the partial neutralisation of the charges of the monomer and of the growing radical in the range of high concentrations of the monomer salt. An analogous effect has been observed after the addition of a neutral salt. On the other hand, in a dilute solution the ionisation of the reaction components, leading to their mutual repulsion, lowers the rate of chain propagation. At the same time, one must not fail to take into account the influence of the ionisation of radicals also on the rate of the bimolecular chain termination. This effect has been observed in the radical polymerisation in water of another anionic monomer—sodium 2-sulphoethyl methacrylate.[34] The increase in the ratio $k_p(fk_{dec})^{0.5}/k_t^{0.5}$ (Fig.4) of the rate constants for the decomposition of the initiator (k_{dec}), chain propagation (k_p), and chain termination (k_t) (where f is the initiation factor), which has been observed experimentally following a decrease of the monomer concentration and is usually for radical polymerisation, has been explained[34] by the effect of the ionic strength of the solution on the degree of dissociation of the monomer and the growing radical. The decrease in ionic strength owing to the dilution of the solution, leading to an increased degree of dissociation of the ionogenic groups of the monomer and the radical, induces an increase in their effective charge, which should lower both the rate of propagation and the rate of bimolecular chain termination as a result of the mutual repulsion of the reaction components. However, this effect is much more marked for the reaction between two radicals (the calculated effective charge on the macroradical is three), which decreases the rate of chain termination to a greater extent than the rate of chain propagation, as a result of which the overall rate of the process increases. At high monomer concentrations, the lack of dependence of the rate of the process on the concentration of the monomer salt (Fig.4) is associated, according to the authors,[34] with the fact that the polymerisation of the fully undissociated salt is observed. The addition of a neutral electrolyte influences the rate of polymerisation in the same direction as the increase in the monomer concentration (Table 2).

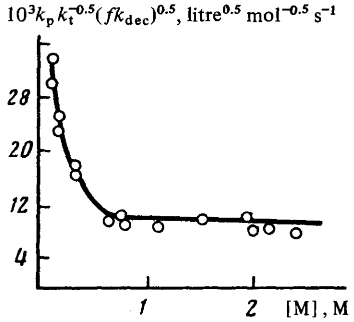


Figure 4. Dependence of the ratio of the rate constants for chain propagation (k_p), chain termination (k_t), and decomposition of the initiator (k_{dec}) on the monomer concentration in water in the radical polymerisation of sodium 2-sulphoethyl methacrylate at 60 °C; f = initiation factor.[34]

The data concerning the influence of a neutral salt on the kinetics of the polymerisation of an anionic monomer obtained in two investigations[34,36] are contradictory. The cause of this should apparently be sought in the different effects of the ionic strength of the solution on the chain propagation and termination rate constants for specific monomers.

The absence of the influence of a neutral salt on the kinetics of the radical polymerisation of derivatives of *NN*-dialkylaminoethyl methacrylate in water at a fixed pH has been observed.[14] For the complete ionisation of the monomer, this phenomenon may be attributed to the increased ability of comparatively hydrophobic polycations to bind low-molecular-weight ions even at a low ionic strength of the solution and thereby abolish the effective positive charge on the end of the chain. Not wishing to dwell especially on the question of the influence of the pH of the solution on the kinetics of the radical polymerisation of ionogenic monomers in water, we refer the reader to Kabanov and Topchiev,[9] who deal with this process in detail.

Table 2. The influence of the concentrations of the monomer and a neutral salt on the ratio of the kinetic constants for the polymerisation of sodium 2-sulphoethylmethacrylate in water at 60 °C.[34]

Monomer, M	$NaNO_3$, M	Ionic strength	$10^3 k_p(fk_{dec})^{0.5}/k_t^{0.5}$, $litre^{0.5}\ mol^{-0.5}\ s^{-1}$
0.12	—	0,12	23.4
0.107	1	1,107	11.9
1.195	—	1.195	10.4

In a number of studies, an increase in the rate of the radical polymerisation of ionising monomers with increased solvent polarity has been noted (including the situation where there is a change from organic to aqueous organic solutions[30, 79–81]). This effect is explained, on the one hand, within the framework of the electrostatic interactions between the reaction components in solution and, on the other, by the association of the monomeric molecules.[81] The influence of the nature of the counterion on the association process and hence on the kinetics of the polymerisation of ionogenic monomers in water has also been noted.[82]

The polymerisation of a series of ionic monomers, namely metal *p*-styrene-, ethylene-, and 2-propene-sulphonates, has been described.[36,83]

In considering the polymerisation in aqueous solutions of ionogenic monomers with a low surface activity, account must be taken of the fact that these systems occupy an intermediate position between true isotropic solutions and colloidal dispersions. The kinetic effects observed in polymerisation in such systems are therefore complex and their interpretation is largely contradictory. On the one hand, a number of features can be accounted for within the framework of the kinetics of homophase reactions when account is taken of the state of the ionogenic groups of the reactants (monomers, radicals). On the other hand, facts appear which do not fit within this framework and require the assumption of the possibility of the association of the monomeric molecules. One may expect that, on passing to typical surface-active monomers, the association effects will predominate and will determine the characteristics of the kinetic behaviour of such systems.

IV. POLYMERISATION IN MICELLAR DISPERSIONS OF SURFACE-ACTIVE MONOMERS

According to the general colloidal-chemical ideas concerning the behaviour of surfactants in water, one may assume that in the case of SAM, whose molecular structure is similar to that of typical organic micelle-forming surfactants, the formation of monomeric molecule–micelle associated species will be observed at SAM concentrations in water above the CCM. On the one hand, the appearance of micelles is reflected in a series of physicochemical characteristics of the system (viscosity, light scattering, surface tension, etc.[70,84,85]) and, on the other, it can alter significantly the rates of many organic reactions in solution.[1,2] This served as a basis for the hypothesis that many characteristics of the SAM polymerisation process in water are also associated with the formation of monomer micelles.[27]

One of the first examples of the polymerisation of monomers of this kind has been the polymerisation of the sodium salts of the allyl esters of α-sulphopalmitic and α-sulphostearic acids.[37] Preliminary experiments showed that the above compounds are able to reduce considerably the interfacial tension, i.e. are typical surfactants. Their radical polymerisation yielded water-soluble polymers with an average degree of polymerisation of 10.

The micelle-forming properties of vinylimidazolium salts and polymers based on them have been investigated.[86,87] With increase in the length of the aliphatic chain in the monomer and the polymer, a transition is observed from the water-soluble to micelle-forming surfactants. The appearance of micelle-forming properties in polymers has been observed for a shorter alkyl substituent than in monomers, which indicates that the polymers are more hydrophobic than the corresponding monomers.

A study of the radical copolymerisation of the above monomers with vinylpyrrolidinone in water and ethanol revealed[88,89] that, for vinyl imidazolium salts, the tendency to add to "its own" radical is significantly greater for the monomer whose molecule contains a longer aliphatic substituent and hence exhibits a greater surface activity. It has been suggested that this is a consequence of the formation of associated species (micelles) in the SAM solution. The enrichment of the micelles in the vinylimidazolium SAM compared with vinylpyrrolidinone should promote the preferential incorporation of the former in the copolymer. On the other hand, the relatively low solubility of vinylpyrrolidinone in the hydrophobic part of the micelles reduces its contribution to the final product. The copolymerisation of vinylimidazolium salts with other monomers (styrene, acrylates) has also been described.[89]

A study of the radical polymerisation of methacryloyloxyalkylammonium salts with an alkyl fragment of equal length showed that in certain cases the effects associated with the ionic character of the SAM may have a greater influence on the polymerisation kinetics in solution than the association phenomenon.[90,91] The rate constant ratio $k_p(fk_{dec})^{0.5}/k_t^{0.5}$ increased with decrease in the monomer concentration in solution to a greater extent the shorter was the length of the alkyl chain in the monomer (Fig.5). Measurements of the electrical conductivities of solutions of monomeric salts at different concentrations characterise the SAM indicated as electrolytes rather than detergents. At the same time, the "open chain" association of the monomeric molecules is not ruled out.[91] The increased rate constant ratio quoted above with decreased concentration of the monomeric salt having the hexyl substituent (Fig.5) as well as the analogous phenomenon for the sodium salt of 2-sulphoethyl methacrylate (Fig.4) have been attributed to a more significant decrease in k_t compared with k_p as a result of the dissociation of the ionogenic groups of the monomer and of the growing radical on dilution.[90] The absence of this effect in the polymerisation of the monomer having the ethyl fragment has been explained by the decrease in the effective charge on the ammonium group as a result of its interaction with the unshared electron pair of the oxygen atom.

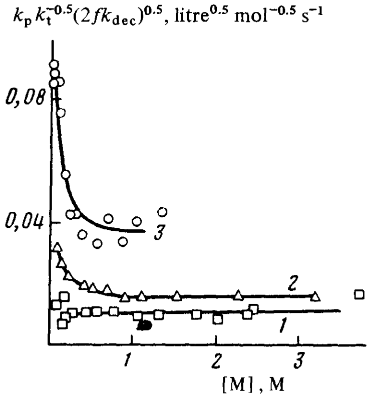


Figure 5. Dependence of the rate constant ratio for the radical polymerisation of compounds of the series $[CH_2{=}C(CH_3){-}COO(CH_2)_n{-}\overset{+}{N}(CH_3)_3]Cl^-$ at 60 °C on the monomer concentration in water:[90] 1) $n = 2$; 2) $n = 3$; 3) $n = 6$.

At the same time, Ringsdorf and Thunig[90] virtually rule out the possible influence of the aggregation of the monomeric molecules on the polymerisation process and fail to explain the increase in the rate constant ratio in the series of monomers with increase of n from 2 to 6 (Fig.5). One of the most probable causes of this effect may be association of the SAM solution at $n = 6$. Plots of $V_p/[In]^{0.5}$ against [M], where [In] is the initiator concentration, obtained in the study of the influence of the monomer concentration $[M]_0$ over a wide range of the latter on the rate of the process V_p, have breaks (Fig.6) whose nature has not been discussed.[91] Other workers[94,95] observed a similar effect and have attributed it to association phenomena (the arrangement of associated species) involving the monomeric molecules in solution (see below).

In contrast to the substance-initiated polymerisation considered above, the spontaneous polymerisation of methacryloyloxyalkylammonium salts in water, which has been shown to have a radical mechanism, has been described.[91] It was found that the order of the polymerisation reaction with respect to the monomer increases with increasing length of the aliphatic chain in its molecule.

The kinetics of the radical polymerisation of vinylpyridinium salts in water has been investigated in a number of studies.[92-95] Fig.7a presents the dependence of the initial rate of polymerisation on the concentration in water of SAM with short and long aliphatic chains in the molecule. Whereas a linear increase in the rate of the process with increasing monomer concentration in the experimental range is observed for the former, for the latter a sharp increase in the slope of the straight line is noted at a certain concentration. It has been shown[94] that the increased rate of the process is accompanied by the increase in the ratio of the propagation rate constant to the square root of the chain termination rate constant, i.e. $k_p/k_t^{0.5}$, and also in the rate of initiation. The correlation of the observed relations with the results of rheological studies on the same SAM solution (Fig.7b) enabled the authors[94] to postulate a relation between the observed kinetic effect and the structural changes in solution.

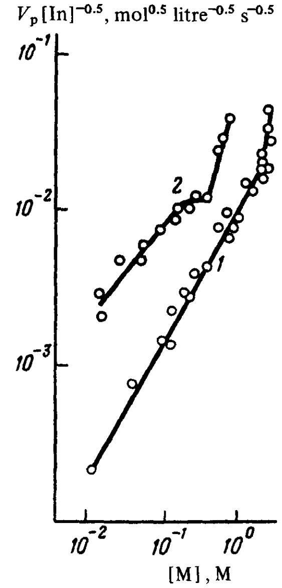
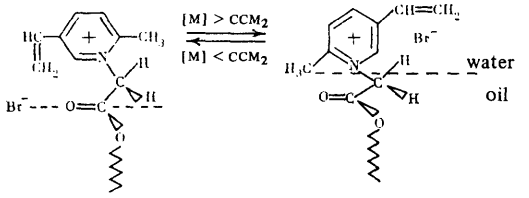


Figure 6. Variation of the ratio of the rate of polymerisation of the monomer $[CH_2{=}C(CH_3)COO(CH_2)_n\overset{+}{N}(CH_3)_3]Cl^-$ to the concentration of the initiator $K_2S_2O_8$ at 60 °C as a function of the initial monomer concentration in water:[90] 1) $n = 2$; 2) $n = 6$.

^{1}H NMR study of the above systems confirmed the hypothesis put forward. Analysis of the chemical shifts showed[93] that, whereas for the monomer with a short chain the presence of only the lowest order associated species may be postulated in the experimental concentration range, for the long-chain monomer multilayer micellar aggregates (lamellae) appear at high SAM concentrations in addition to the spherical micelles. The higher degree of organisation of SAM with an extended aliphatic chain and also the characteristic features of the disposition of the double bonds of the monomer in the micelles, promoting the occurrence of polymerisation, may in fact be the causes of the observed kinetic effect. The application of the ^{1}H NMR method made it possible to determine the conformation of the SAM molecules at the interface in the micelles.[93] The scheme below illustrates the change in the conformation of the molecule as a function of the structure of the associated species:



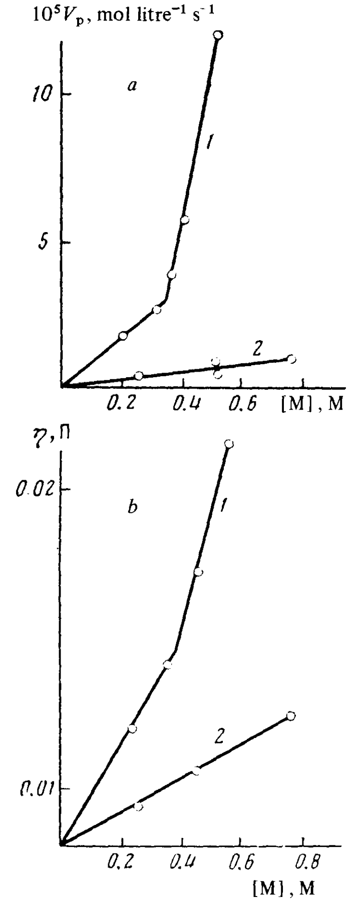
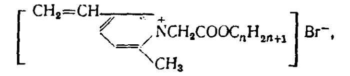


Figure 7. Dependence of the initial rate of polymerisation (*a*) and of the absolute viscosity of solutions of the salts (*b*).[95]



where *n* = 10 (line *1*) and *n* = 4 (line *2*), on the monomer concentration in water.[95]

Subsequently finer kinetic effects, occurring in the radical polymerisation of cationic SAM in water, were observed. Thus in a study of aqueous dispersion of SAM based on methacryloylethylammonium and allylammonium salts, it was found[96,97] that, in the region corresponding to the existence of micellar solutions, the plot of the dependence of the initial rate of polymerisation on the monomer concentration has three sections: a initial linear growth section, a middle section with a constant rate, and then a new section corresponding to growth (Fig. 8*a*). Three linear sections with different slopes are also observed on the plot of the viscosity of aqueous monomer solutions against concentration (Fig. 8*b*). The satisfactory agreement between the concentrations at the points of inflection on the rheological curves and on the "rate–monomer concentration" plots is striking. These data were interpreted as follows.[97] The initial section corresponding to an increasing rate of the process appears as a result of the increase in the total amount of the monomer in the system, in the first place within the spherical micelles, which are responsible for the process kinetics in the experimental SAM concentration range (two orders of magnitude larger than the CCM). The section with a constant rate corresponds to the appearance in the system of anisotropic SAM micelles (confirmed by the ^1H NMR method[96]), in which there is virtually no polymerisation (it is observed only in the spherical micelle phase). According to the authors,[97] this is associated with the disposition of the double bonds of the monomer in the associated species indicated which is unfavourable for polymerisation. The subsequent increase in the rate of the process with increasing concentration is a consequence of the appearance in the dispersion of SAM asssociated species with a high level of organisation, namely aggregates of micelles—multilayer lamellae. The mutual approach of the surfaces of neighbouring micelles in such lamellae induces an increase in the effective concentration of the double bonds of the monomer in the reaction zone and a change in their relative positions.

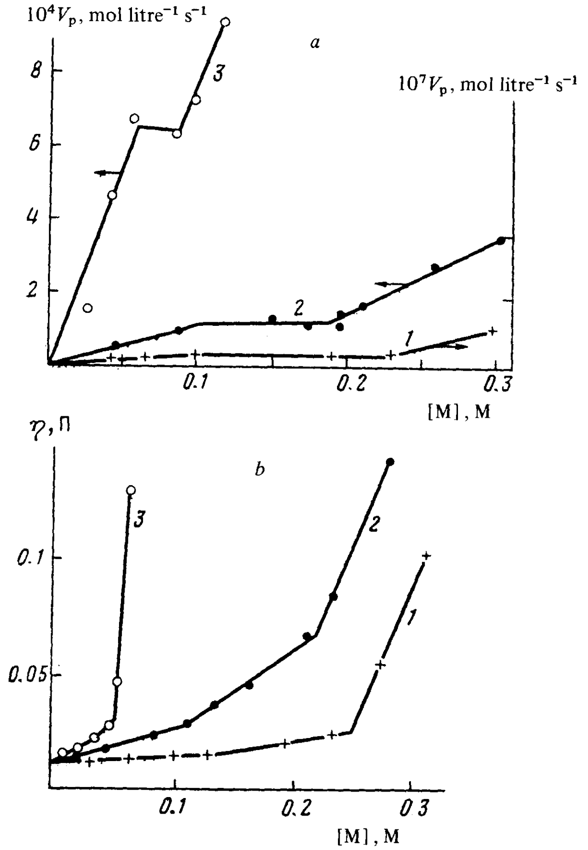
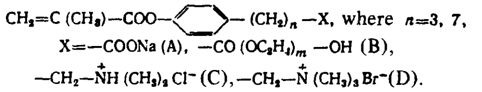


Figure 8. Dependence of the monomer concentration in water in the initial rate of polymerisation at 70 °C (*a*) and of the absolute viscosity at 40 °C of solutions of different salts[19] (*b*) 1) $[(CH_2{=}CH{-}CH_2)_2\overset{+}{N}(CH_3)CH_2COOC_{12}H_{25}]Br^-$; 2) $[CH_2{=}C(CH_3)COOC_2H_4\overset{+}{N}(CH_3)_2CH_2COOC_{12}H_{25}]Br^-$; 3) $[CH_2{=}C(CH_3)COOC_2H_4\overset{+}{N}(CH_3)_2CH_2COOC_{16}H_{25}]Br^-$.

The intrinsic viscosities of polymers in all three SAM concentration ranges have been published.[97] The agreement between these values for the products corresponding to the first and second sections supports the view that at these monomer concentrations the process takes place in the same phase, namely in the spherical micelles. The increase in the viscosity of the polymer on passing to the third section is an argument in support of the appearance in the system of SAM aggregates more complex than the micelles and with a higher degree of association (lamellae). Electron microscopy data for the specimens after polymerisation confirm these hypotheses.[97] Comparison of data for the polymerisation of cationic SAM of two types—with acrylic and allyl polymerisable groups—shows that, as in the isotropic solution, in the micellar dispersion the first type exhibits a higher activity in the polymerisation process than the second, as a result of which the overall rate of the process is much higher in the former case.[97]

Structural transitions in a micellar SAM dispersion have also been observed for *N*-dodecyl-*N'*-vinylimidazolium iodide.[98] However, the radiation-initiated polymerisation of this monomer at concentrations corresponding to both true and micellar solutions afforded identical yields of polymers having similar solubilities in organic solvents and molecular weights proportional to the initial concentration of the monomer in water. This permitted the conclusion that the association of the SAM has no influence on the morphology and degree of polymerisation of the polymer formed. According to the authors,[98] the polymerisation in the micellar dispersions of the SAM indicated proceeds analogously to the reaction in the isotropic medium (monomer solution). However, this conclusion appears insufficiently convincing owing to the lack of data on the rate of polymerisation. This precludes the estimation of the influence of the association of the monomer on the process kinetics.

The polymerisation in water of monomers with hydrophilic "heads" of different nature has been investigated:[30]



Preliminary experiments showed that all the compounds indicated are surface-active. Their CCM were determined. When the polymerisation of the SAM (C) with $n = 3$ and with $n = 7$ was initiated with potassium persulphate, reaction orders of 0.33 and 0.27 respectively with respect to the initiator were obtained. The low reaction order may be associated with the positive absorption of the persulphate anion on the surfaces of the positively charged SAM micelles. When dimethyl azoisobutyrate (DAI) was used as initiator, the rate of polymerisation of the cationic monomers increased significantly on passing from the true solution in aqueous ethanol to the micellar solution in water.[30] It is suggested that this is associated with the enrichment of the SAM micelles in the oil-soluble initiator.

An increase in the rate of the process has also been observed following an increase in the length of the alkyl chain in the monomer and a decrease in the latter in solution (the range of dilute SAM solutions), which is correlated with the data presented in Fig.5. In concentrated surfactant solutions, the rate of polymerisation depended less on the length of the aliphatic fragment in the monomer than in a dilute solution and hardly changed on formation of monomer micelles in the system. The latter effect has been explained[30] by the fact that the polymeric radical is more hydrophobic than the corresponding ionogenic monomer[86,87] and can therefore form its micelle regardless of the state of the monomer solution (true or micellar) (Fig.9). If it were supposed that the rate of polymerisation is determined solely by the behaviour of the polymeric radicals, then the rate of the process would be independent of the degree of organisation of the monomer over a certain range of the concentrations of the latter. However, this hypothesis is fairly controversial because the influence of the association of the monomeric molecules on the kinetics of polymerisation in micellar SAM dispersions where, as in the case under discussion, the polymeric radicals are present as micelles, has been demonstrated for a large number of examples.[92-97] In reality, it follows from the data of the above study[30] that there is a significant dependence of the rate of polymerisation in the given system on the monomer concentration (Fig.10). The analogy between the relation described and the data of Egorov et al.[97] (Fig.8*a*) suggests a relation between the observed phenomena and the structure formation in the SAM dispersion.

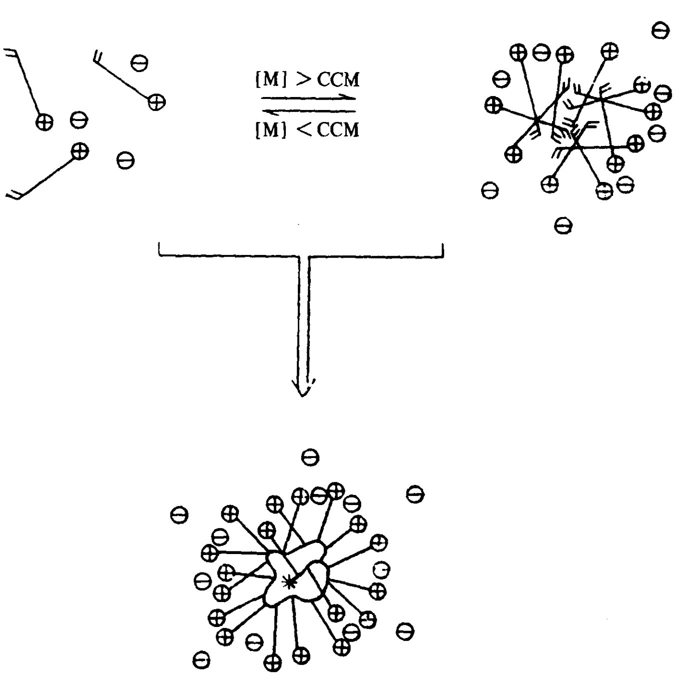
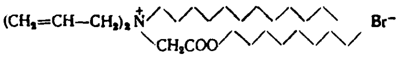


Figure 9. The formation of growth radicals in the polymerisation of methacryloylphenylalkylammonium salts in water.[30]

The radiation-initiated polymerisation of sodium undec-10-enoate in water has been investigated.[41] The polymerisation takes place only at monomer concentrations exceeding the CCM. This is probably associated with the fact that the monomer double bonds are located in the hydrophobic nuclei of the micelles in such a way that this facilitates the polymerisation.

The colloidal properties of monomers, especially micelle formation in the solutions of any cationic, anionic and nonionic polymers which are surfactants, have been investigated in a series of studies.[93,96,99] Structure formation and polymerisation in solutions of monomers which are structural analogues of glycolipids[56,57] and phospholipids[100] have also been described.

Together with single-stranded SAM, cationic monomers based on diallylammonium salts containing two extended aliphatic chains have been investigated:[97]



Since the structure of the above compounds resembles the structure of natural phospholipids, they will henceforth be referred to as lipid-like. The dependences of the initial rate of polymerisation and of the viscosity of the aqueous solutions of the SAM quoted, obtained by simple dissolution, on the monomer concentration in water are analogous to the dependences obtained for the typical SAM with a single aliphatic chain (Fig. 8*a*), which indicates an analogy in the behaviour of the lipid-like and single-stranded SAM in the polymerisation process and hence in the association process and in the rearrangement of the associated monomers in water. As for the usual SAM, the transition from the spherical to the anisotropic monomer micelles with increase in its concentration is accompanied under these conditions by a change in the order of the polymerisation reaction with respect to the monomer from 1 to 0. Further increase in the concentration leads to the appearance of lamellar SAM formations, which induces an additional increase in the rate of the process proportional to the monomer concentration. The explanation of the phenomena indicated, proposed by the authors,[97] is analogous to that quoted above for single-stranded SAM.

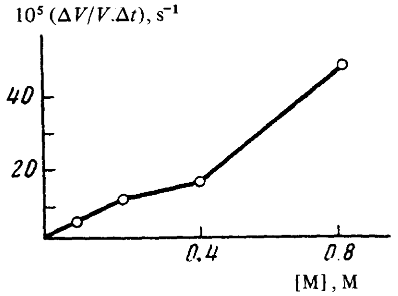
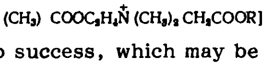


Figure 10. Dependence of the rate of polymerisation of trimethyl[3-(4-methacryloyloxyphenyl)propyl]ammonium bromide in the presence of DAI at 50 °C on the monomer concentration in water according to Siol's data.[30]

On passing from a symmetrical lipid-like monomer (aliphatic chains of similar length) to a monomer with an asymmetric hydrophobic component (with aliphatic substituents appreciably differing in length), the critical concentrations for the rearrangement of the associated species diminish, i.e. the SAM becomes more hydrophobic.[97] This entails an increase in the overall rate of the polymerisation process, which is analogous to the behaviour of the single-stranded SAM with increase in the length of the aliphatic chain in the molecule.

Attempts have been made in a number of studies to fix the structure of the micelles by polymerisation. The use of the monomers


I^- (V) (Ref.98);

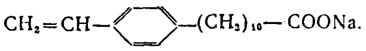
$CH_2{=}C(CH_3)CON(R)-(CH_2)_{10}-COONa$ (VI) (Refs.27, 38);

$CH_2{=}C(CH_3)CON(R)-(CH_2)_{10}-CO(OC_2H_4)_5-OCH_3$ (VII) (Refs.27, 38);

$[CH_2{=}C(CH_3)COOC_2H_4\overset{+}{N}(CH_3)_2CH_2COOR]Br^-$ (VIII) (Ref.19).

did not lead to success, which may be associated, for example, with the need to employ large amounts of the initiator, as in the case of the monomers (VI) and (VII), which polymerise at a slow rate.[27]

It has been noted[27] that one of the first positive results was obtained in the polymerisation of the compound



The polymer obtained had a micellar structure, which was achieved by introducing a cross-linking agent.

Another example of the preparation of polymeric micelles has been described in studies[41,102] of the polymerisation of sodium undec-10-enoate: $CH_2{=}CH(CH_2)_8COONa$. Below the CCM, this monomer is incapable of homopolymerisation, but above this concentration the process proceeds with formation of macromolecules, whose degree of polymerisation is equal to the number of SAM molecules aggregated in the micelles. NMR data confirm the fixation of the micellar structure on polymerisation.

In the study quoted above,[97] it was possible to achieve the fixation of not only spherical micelles but also of lamellar formations, by polymerising the monomer $(CH_2{=}CH-CH_2)_2.\overset{+}{N}(CH_3)CH_2COORBr^-$, which was confirmed by electron microscopy.

Analysis of data on the fixation of SAM micelles by polymerisation shows that a positive result has been achieved either by using monomers with a double bond whose reactivity is low in the polymerisation process or by the introduction of an additional cross-linking agent.

Thus the polymerisation of SAM in aqueous micellar dispersions differs from solution (homogeneous) polymerisation by a number of features associated in the first place with the influence of structure formation in the monomeric molecules on the process kinetics and on the macrostructure of the polymer formed. We may note that there are systems where this influence cannot be traced in an explicit form. The appearance of SAM micelles in the solution induces as a rule an increase in the overall rate of polymerisation. This is associated, on the one hand, with the increase in the local monomer concentration in the associated species compared with the isotropic solution. On the other hand, a change in the elementary reaction constants and also in the reaction order with respect to the initator (for example, as a result of the concentration of the latter on the oppositely charged interface) or with respect to the monomer (for example, as a result of a change in the relative positions of the SAM molecules on passing from the true solution to the associated species) has been observed. Presumably the role of the latter factor increases significantly on passing to structural SAM formations with a higher level of organisation than in micelles, such as vesicles (as a rule made up of monomers whose molecular structure is similar to that of natural phospholipids) or highly organised monolayers of monomers at the water–air interface. Yet another factor influencing the polymerisation kinetics in such systems is the formation of polymeric radicals in the form of individual micelles separated by an electrostatic barrier. This should increase the overall rate of the process compared with the system where the polymer exists in the form of a true solution, as a result of the decreased contribution by the bimolecular chain termination. This has been demonstated, for example, in a study[100] where the radicals were induced directly in the surfactant micelles.

Together with the micelle formation proper, the SAM polymerisation reaction in water can depend significantly on the growth and rearrangement of the monomer micelles and on the appearance of associated species with a higher level of organisation (lamellae). In a number of instances it has been possible to fix this structure of the SAM associated species by polymerisation, but so far this is an exception rather than the rule.

V. POLYMERISATION IN LIPOSOMES AND MONOLAYERS OF SURFACE-ACTIVE MONOMERS

This field has been developing vigorously in recent years, as shown by the progressive increase in the number of communications devoted to monomeric and polymeric monolayers and liposomes. A number of reviews describe fairly completely the state of affairs in this field.[16,27,103] We shall deal with the factors which are important in the context of the present article. This concerns the kinetic effects in the polymerisation process in monolayers and vesicular SAM dispersions.

The study of the polymerisation conditions in a monolayer[55] showed the advantage of UV initiation over chemical initiation, the need to eliminate atmospheric oxygen, etc. It has been established in relation to the $CH_2{=}C(CH_3)COOC_{18}H_{37}$ monomer that an increase in the lateral pressure, leading to a change (ordering) of the monomer monolayer structure at the water–gas interface, may promote or hinder the polymerisation process (Fig.11*a*). It is seen from Fig.11*a* that, with increase in the external pressure, the rate of polymerisation initially increases and above a certain critical pressure it begins to decrease. The observed phenomena have been explained in the following manner.[55] At a low lateral pressure, the monomer in the disordered state (A) (see scheme in Fig.11*b*) forms the polymer (D) at a low rate. With increase in the pressure, the monomer passes to the ordered state (B), the rate of polymerisation increases, and the polymer with the structure (E) is the result. Further increase of the pressure leads to the state (C) in which the monomer is incapable of polymerisation owing to steric hindrance.

An analogy can be seen between the effects observed in the transition from the monomer state (B) to (C) and the data obtained in a study[97] where a change in the order of the polymerisation reaction with respect to the monomer from first to second was observed on passing from spherical to anisotropic monomer micelles (as the aqueous SAM solution was concentrated) during the ordering of the SAM associated species (Fig.8*a*). The observed effect has also been discussed from the standpoint of the dispositions of the monomer molecules at the interface in the associated species which are favourable and unfavourable for polymerisation.

It has also been noted[104] that, with increase in the lateral pressure in the octadecyl methacrylate monolayers, an increase in the rate of polymerisation is observed. Cases are known where the increase in the lateral pressure induces a decrease in the rate of polymerisation.[105] These phenomena can be explained within the framework of the scheme presented above.

It has been observed[39,106,107] that polymerisation in monolayers of monomers of a series of diacetylenic carboxylic acids of the type $CH_3{-}(CH_2)_n{-}C{\equiv}C{-}C{\equiv}C{-}C_8H_{16}COOH$ occurs at 20 °C if n is 11–15 and at 2 °C if $n = 9$ and does not occur at all if $n = 4$–7. The salts of the above acids with the Na^+ and K^+ counterions polymerise at high pH and those with Li^+ and bivalent cations are incapable of polymerisation under these conditions, which is associated, according to the authors,[106,107] with the differences in the packing densities of the monomers in the monolayer. It is of interest to note that the salts containing Li^+ are able to polymerise at pH < 6. It is believed that this induced by a rearrangement of the associated monomer species and that in this instance a polymer having a regular structure is formed. The retention of order in the monolayers in the polymerisation process has also been noted in a number of other studies.[40,108–109]

Two studies have been devoted to aqueous dispersions of liposomes obtained from cationic monomers based on diallylammonium salts.[96,97] The rate of radical polymerisation of monomers with two extended aliphatic chains in the molecule (lipid-like monomers), initiated by the thermal decomposition of DAI, increases overall on passing from dispersions obtained by simple dissolution of the monomer in water, to systems

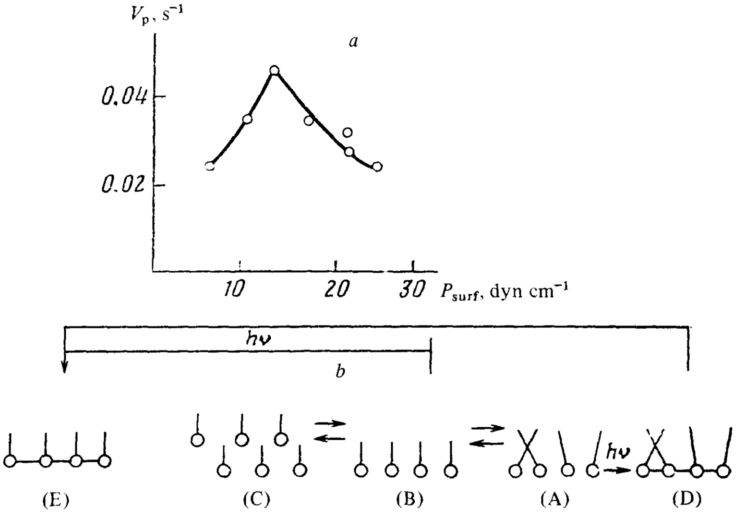
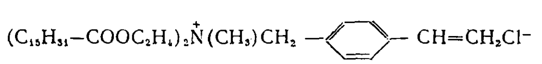


Figure 11. The behaviour of octadecyl methacrylate in the polymerisation process in a monolayer at the water–nitrogen interface at 23 °C and at different surface pressures:[55] *a*) pressure dependence of the rate of polymerisation: *b*) schematic illustration of behaviour: the arrows directed to the right correspond to a decrease of surface pressure and those directed to the left correspond to its increase; the symbol $\xrightarrow{h\nu}$ denotes polymerisation under the influence of radiation.

formed by dispersing the monomer with the aid of ultrasound. The inflections in the plots of the viscosity of the solution against the monomer concentration, which correspond, as mentioned above, to a rearrangement in the colloidal SAM dispersions, then vanish. At the same time it is known[110] that, when aqueous dispersions of lipids and their synthetic analogues are dispersed with ultrasound, the formation of liposomes is observed. All this enabled the above investigators[96, 97] to interpret the results as follows. Ultrasonic treatment of aqueous dispersions of diallylammonium lipid-like SAM leads to the formation of monomer liposomes, in which the level of organisation of the molecules is significantly higher than in the micelles. In the first place, in the liposomes the effective monomer concentration is higher and the disposition of the double bonds is more favourable, which increases the overall rate of the process. At the same time, one cannot fail to take into account the possible decrease in the chain termination rate constant as a result of the formation of highly organised layers, where the mobility, in the first place lateral mobility, of the molecules themselves and even more so of the polymeric radicals is significantly lower than in the micelles. The virtual identity of the initial sections of the plots of the rate of polymerisation against the monomer concentration for a micellar solution and a dispersion of liposomes suggested the possibility of the spontaneous formation of liposomes-like structures at comparatively high monomer concentrations in water, which had been established earlier for dispersions of the given SAM at a low concentration.[111] The existence of lamellar and liposome structures of these SAM in the monomer dispersion and their fixation on polymerisation have been confirmed by electronic spectroscopy.[112]

In respect of the lipid-like ammonium monomer

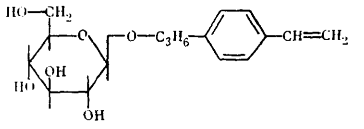


it has been shown[113] that the rate of radical polymerisation increases significantly on passing from the isotropic solution in ethanol to a vesicular dispersion (in water) as a consequence of the orientation of the monomer in the structure of the vesicle.

Thus, in the case of double-stranded lipid-like SAM, the kinetics of the polymerisation process in micellar dispersions, known for single-stranded SAM, is reproduced, on the one hand, and the appearance of higher-order structures, structurally similar to the liposomes of natural lipids, becomes possible on the other hand. The kinetics of polymerisation in such structures are determined primarily by the very high degree of order in their monomer units, which entails as a rule a high rate of the process. Another characteristic feature of these systems, compared with micellar systems, is the possibility of their fixation by polymerisation, which is almost independent of the monomer structure (only the negative influence of the size of the counterion has been noted), of the activity of its polymerising group, and also of the method of initiation. The extremely high stability (with respect to time and mechanical and other influences) of the newly formed polymeric liposomes compared with the initial monomeric liposomes, which has been noted in a number of publications,[75,103,114–116] leads to extensive possibilities for their application.

VI. PROSPECTS FOR THE ULTILISATION OF SURFACE-ACTIVE MONOMERS

The first studies on the synthesis of monomers of this new class and their polymerisation in an aqueous medium had a purely applied aim—the preparation of colloidal (micellar) surfactant structures fixed by means of polymerisation. This provided a reliable method for the investigation of the shape and structure of the micellar formations. Furthermore, the new surfactant structures proved to be effective in the investigation of the microstructure of associated species. For example, the use of a monomer containing simultaneously glycoside and styrene groups,[56] i.e.



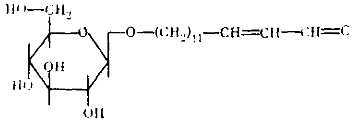
gave definite advantages in the study of the influence of the concentration of aqueous SAM solutions on association processes (rearrangement of the associated species) involving monomers, especially in the testing of changes in the microstructure of micelles.

The fixation of micellar structures by means of the polymerisation of SAM undoubtedly has a practical value, apart from its purely theoretical importance, especially for the synthesis of ion-exchange resins, carriers for medicinal and biological preparations, etc.

One of the most vigorously developing fields has been recently the synthesis of lipid-like SAM and their use for the preparation of polymeric analogues of biomembranes in the form of monolayer films, liposomes, and vesicles,[16,37,40] for the modelling with their aid of membrane processes,[16] and for the incorporation (inclusion, grafting) in the polymer of biological and medicinal preparations,[17,27] used in biology, biotechnology and medicine.

The synthesis of SAM by the modification of natural lipids[117] and other natural products[118] is of special interest. It is apparently possible to obtain in this way SAM capable of imparting a whole spectrum of unique properties of natural objects to polymers as a result of homopolymerisation and copolymerisation.

Thus it has been shown[57] that the inclusion in phospholipid liposomes of a monomer containing a carbohydrate fragment, i.e.



and its subsequent polymerisation make it possible to obtain stable models of biological membranes capable of surface "recognition" by the corresponding proteins.

Overall, the chemistry of SAM is still in the initial stage of its development. However, the likely usefulness of these objects for the solution of a whole series of problems in theoretical and practical chemistry, biology, and medicine has already been demonstrated. Presumably the development of this field will extend the existing applications of SAM and will create new ones.

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The Influence of Ligands on the Catalytic Properties of Nickel-containing Systems in Oligomerisation and Polymerisation Reactions

A.G.Azizov

The results of studies on the activating influence of ligands on the catalytic properties of nickel-containing systems in oligomerisation, co-oligomerisation, and polymerisation reactions are surveyed and the electronic and steric aspects of this phenomenon are analysed from the standpoint of an S_ECi mechanism. The possibility of a homolytic and heterolytic activation of the Ni-C bond in catalytic centres by electron-accepting and electron-donating ligands respectively is examined. It is shown that the molecular weight of the oligomerisation and polymerisation products is determined by the steric effect of the ligands and that the stability of the catalytic centres depend primarily on the frequency of the active centre ⇌ potential centre transitions.

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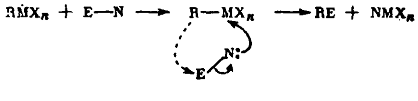
I. INTRODUCTION

In the presence of nickel-containing catalysts it is possible to obtain a broad spectrum of oligomers and polymers of unsaturated hydrocarbons. The composition, structure, and molecular weight of these products depends on the nature of the monomers, the ligand environment of the nickel in catalytic centres, the composition of the catalyst, and the reaction conditions.[1-6] It is now generally recognised that the active centres in nickel-containing catalysts for linear dimerisation, oligomerisation, and polymerisation are in most cases organometallic and hydride derivatives of nickel.[1-7] However, these compounds by themselves exhibit only an insignificant activity. Their catalytic action is greatly enhanced in the presence of electron-accepting additives capable of increasing the effective positive charge on the nickel atom as a result of the formation of charge-transfer complexes on an anion.[1] The influence of electron-donating additives in different reactions is manifested in different ways: they reduce the activity and stereoselectivity of the action of the catalyst in diene polymerisation processes, while in olefin dimerisation and codimerisation reactions they increase its activity and stability.[4-8]

There is as yet no unique approach in the literature to the explanation of the mechanisms of the activating influence of ligands on the catalytic properties of nickel-containing systems in various reactions. This is apparently associated with the fact that, although the studies by individual groups of investigators do cover a broad range of catalytic properties, each separate study was devoted to the investigation of the behaviour of nickel-containing systems only in specific reactions. The mechanisms of the formation and destruction of the active centres, and the role of the electronic and steric factors in the activation of nickel-containing systems and in the formation of the structures and the establishment of the molecular weight of the oligomerisation and polymerisation products have not been ultimately elucidated. The elucidation of these fundamental questions requires a comparative analysis of the activating influence of ligands on the catalytic properties of the same systems in different reactions and, conversely, on different systems in a single standard reaction.

Valuable information about the role of electronic and steric effects of ligands can be obtained by the systematic study of their influence on the kinetic parameters of the elementary stages of the reactions in the transition from dimerisation and codimerisation to oligomerisation and polymerisation of unsaturated hydrocarbons. Evidently, the model reactions should then be selective to the maximum possible extent and readily controllable. The highly selective oligomerisation and co-oligomerisation reactions with α-olefins of styrene and its derivatives, which occupy an intermediate position between olefins and dienes[1,5] as regards their polymer-forming capacities, are convenient objects of study.

In the present review, the experimental data are analysed on the basis of ideas about the electrophilic mechanisms of the reactions of organometallic compounds proceeding via the nucleophilic coordination of the substrate to the metal atom with subsequent electrophilic attack on the negatively charged α-carbon atom in a many-centre cyclic transition state. A similar mechanism, called the S_ECi mechanism was proposed previously,[9] for substitution and addition reactions between organometallic compounds of non-transition metals and E—N electrophiles, which consist of electrophilic (E) and nucleophilic (N) components:



$$RMX_n + E{-}N \longrightarrow R{-}MX_n \longrightarrow RE + NMX_n$$

An analogous mechanism can be used also in discussing the reactions involving the addition of unsaturated hydrocarbons to organometallic and hydride derivatives of nickel. These reactions are the key stages in the oligomerisation and polymerisation processes. Indeed, it has now come to be assumed that the addition of unsaturated hydrocarbons to hydride and organometallic centres takes place in two stages: (1) the formation of an intermediate π-complex with the transition metal and (2) the subsequent insertion of the coordinated olefin molecule via a polar cyclic transition state.

According to the Dewar–Chatt–Duncanson model, the binding of olefins to the metal in the π-complexes is achieved as a result of the direct donor–acceptor and the reverse dative interactions.[10,11] The contribution of the dative interaction diminishes with increase of the degree of oxidation of the complex-forming metal and is minimal for high degrees of oxidation of the metal.[12] This means that the π-complex formation processes at the nickel(II)-containing active centres is a nucleophilic reaction in the sense in which it has been considered by Moiseev.[13,14] On the other hand, in the coordinated state, the olefin molecule acquires the capacity for electrophilic attack,[15] because the partial charge appearing on it as a result of the donor–acceptor interaction is not fully compensated by the dative interaction. Under these conditions, in the many-centre transition state the *d* orbitals of the metal and the sp^3 orbitals of the α-carbon atom (or the *s* orbitals of hydrogen) interact with the bonding orbitals of the olefin.[16–18] As a result, the thermal addition reaction is symmetry-allowed or, according to Pearson's terminology, is partly prohibited.[19]

The formal analogy with the S_ECi mechanism is manifested by the fact that the nucleophilic attack on the transition metal atom by the substrate molecule takes place before its electrophilic insertion in the polarised $R^{\delta-}$–$M^{\delta+}$ bond via an intermediate cyclic transition state. Consequently, one can assume that the characteristics of the reactions involving the addition of an olefin (diene) to organometallic and hydride derivatives of nickel should not differ significantly in their character from the characteristics of the reactions involving the S_ECi mechanism. In this case, the opposite effects of the ligands on the catalytic properties of nickel-containing systems in dimerisation reactions, on the one hand, and in oligomerisation (polymerisation) reactions, on the other, can be accounted for by the different nature of the rate-limiting stages in these processes. Analysis of the experimental results confirms this hypothesis.

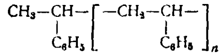
II. THE INFLUENCE OF LIGANDS ON THE MOLECULAR WEIGHT OF OLIGOSTYRENE AND THE CHARACTER OF THE CHAIN TERMINATION IN THE OLIGOMERISATION OF STYRENE

It has been shown[20–23] that the degree of polymerisation of styrene in the presence of π-alkenylnickel halides depends on the nature of the halide ion. Thus π-crotylnickel iodide induces the formation of the styrene dimer (1,3-diphenylbut-1-ene), while the bromide and chloride complexes lead to the formation of oligostyrenes with average degrees of polymerisation of 5–6 and 8–12 respectively. An even greater increase in the length of the chain (up to 200–500 units) is attained when electron acceptors such as $MnCl_2$ and $Ni(OCOCCl_3)_2$ are introduced into the system.[22]

The molecular weight of the styrene oligomerisation products in the presence of systems of the Ziegler–Natta type also depends on the catalyst.[24] The two-component system containing *NN*-diethyldithiocarbamate or nickel *OO*-dialkyl (or *OO*-diaryl) phosphorodithioate and diethylaluminium chloride directs the process towards the formation of a dimer, while the additional introduction of a phosphorus-containing ligand (phosphine, phosphite) results in the formation of oligomers with an average degree of polymerisation of 4–9. This difference between the two- and three-component systems is due to the change in the character of chain termination in the presence of a phosphorus-containing ligand in the coordination sphere of nickel: instead of spontaneous chain transfer (β-elimination), the chain is transferred to the monomer, which increases the average degree of polymerisation. Comparison of the results of Azizov et al.[25] with the data of Makovetskii and co-workers[20–22] shows that the introduction of both electron-accepting and electron-donating ligands can increase the molecular weight of the styrene oligomerisation products.

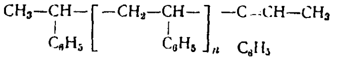
III. THE SELECTIVITY OF THE CO-OLIGOMERISATION REACTIONS OF STYRENE WITH ETHYLENE AND PROPENE

In the co-oligomerisation of styrene with α-olefins, the latter add "head to tail" and "tail to tail". The structure of the products of the reaction with participation of ethylene corresponds to formulae (I) and (II) and that of the products of the reaction involving propene corresponds to formulae (III) and (IV):



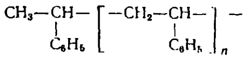
$$CH_3-\underset{C_6H_5}{CH}-\left[-CH_2-\underset{C_6H_5}{CH}-\right]_n-CH=CH_2$$

(I)



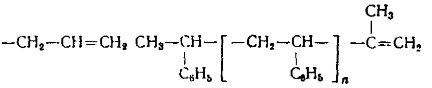
$$CH_3-\underset{C_6H_5}{CH}-\left[-CH_2-\underset{C_6H_5}{CH}-\right]_n-\underset{C_6H_5}{C}=CH-CH_3$$

(II)



$$CH_3-\underset{C_6H_5}{CH}-\left[-CH_2-\underset{C_6H_5}{CH}-\right]_n-CH_2-CH=CH_2$$

(III)



$$CH_3-\underset{C_6H_5}{CH}-\left[-CH_2-\underset{C_6H_5}{CH}-\right]_n-\overset{CH_3}{C}=CH_2$$

(IV)

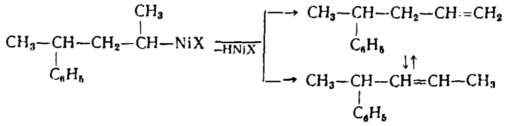
The products (I)–(III) are formed as a result of the "head to tail" addition, while the product (IV) results from the "tail to tail" addition. In the limiting case, where $n = 0$, the product of the co-oligomerisation of styrene with ethylene is 3-phenylbut-1-ene and those of the co-oligomerisation with propene are 4-phenylpent-2-ene, 4-phenylpent-1-ene, and 2-methyl-3-phenylbut-1-ene (2-M-3-PB-1).[25,26]

In contrast to the codimerisation of other pairs of the lowest olefins (for example, ethylene and propene[4,5,7]), in the codimerisation of styrene with ethylene[19] only a single product, namely 3-phenylbut-1-ene, is formed up to appreciable degrees of conversion. For very high conversions, 2-phenylbut-1-ene isomerises to 2-phenylbut-1-ene. The curve for the accumulation of 3-phenylbut-1-ene as a function of time therefore passes through a maximum, which corresponds to 80–100% conversion of styrene.[8,19] The nature of the components of the catalytic system has a considerable influence on the process selectivity. The highest yield of 3-phenylbut-1-ene (100%) is observed in the presence of catalytic systems based on organic dithio-derivatives of nickel (dithiocarbamate, phosphorodithioate).[24,27] The dimerisation of ethylene in the presence of a tertiary phosphine or a phosphite in the catalyst is appreciable only for a high degree of conversion of styrene (>90%). When a two-component system is used, the yield of 3-phenylbut-1-ene falls sharply with respect to both monomers which have reacted (it is particularly marked with respect to the ethylene which has reacted) compared with the three-components systems.[8,25,28] 3-Phenylbut-1-ene isomerises after the complete conversion of styrene.

The yields of the reaction products pass through a maximum also in the codimerisation of *p*-chlorostyrene and vinyltoluene with ethylene. On the other hand, in the codimerisation of α-methylstyrene with ethylene isomerisation is not observed and the yield of 3-methyl-3-phenylbut-1-ene corresponds fully to the consumption of α-methylstyrene.[25]

The codimerisation of styrene with propenes takes place both "head to tail" and "tail to tail". The former type leads to the formation of a mixture of 4-phenylpentenes and the latter to the formation of 2-methyl-3-phenylbut-1-ene. In certain cases propene dimers, phenyloctenes, and styrene oligomers are also formed.[27-30] In the given case the selectivity of the codimerisation also depends, other conditions being equal, on the nature of the components and on the composition of the catalyst: in the presence of two-component systems, an appreciable amount of styrene (up to 42%) is converted into oligomers and co-oligomers. Dithio-systems ensure the exclusive formation of codimers—phenylpentenes (PP). Up to the complete conversion of styrene, they catalyse the addition of the monomers of the "head to tail" type only and, in contrast to acetylacetonate systems, the increase of the Al:Ni ratio to 200:1 does not lower the selectivity of their action.[29,30]

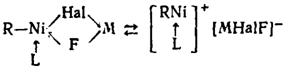
Regardless of the nature of the catalyst components, the 4-PP-1 and 4-PP-2 codimers are formed from the very beginning of the process, which is consistent with the hypothesis of their formation from the same intermediate as a result of β-elimination reactions via different pathways:



$$CH_3-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-NiX \xrightarrow[-HNiX]{} \begin{cases} CH_3-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-CH{=}CH_2 \\ \quad\downarrow\uparrow \\ CH_3-\underset{C_6H_5}{\underset{|}{CH}}-CH{=}CH-CH_3 \end{cases}$$

However, the isomerisation of 4-PP-1 to 4-PP-2 also takes place during the process. The isomerisation continues further after the formation of 2-PP-2. In contrast to 4-PP-1, 4-PP-2 isomerises to 2-PP-2 only after the complete conversion of styrene. This fact, together with the low rate of isomerisation of 3-phenylbut-1-ene, indicates a decrease of the rate of isomerisation as the double bond is located closer to the benzene ring. Comparison of the results of a thermodynamic calculation of the equilibrium composition of phenylpentenes with experimental data leads to the same conclusion.[29,30] Regardless of the nature of the catalyst components, the yield of 4-PP isomers for any degree of conversion of styrene greatly exceeds their maximum equilibrium concentrations, which are 0.1% for 4-PP-1, 72% for *trans*-4-PP-2, and 15% for *cis*-4-PP-2 at 10–50 °C. With increase of the degree of conversion, the content of 4-PP-1 in the codimerisation products diminishes, approaching the equilibrium value, while that of 4-PP-2 increases to 50–95 wt.%. The yield of 2-PP-2 (1–9%) is much smaller than the theoretical value (28–94%), which is due to the slow isomerisation of 4-PP-2.

The nature of the organoaluminium compound has a significant influence on the yield of the codimerisation products.[27] Catalytic systems based on triethylaluminium and not containing activating additives have a very low efficiency. When CH_2Cl_2, $AlCl_3$, $TiCl_4$, $BF_3.(C_2H_5)_2O$, and $C_2H_5AlCl_2$ are introduced into such systems, the rate of the process and the overall yield of the codimerisation products increase sharply, indicating that the most active codimerisation centres contain electron-accepting ligands or the products of their interaction with the organoaluminium compounds. This postulate is confirmed by the results of studies[31,32] of the interaction of the components of the $Ni(acac)_2 + P(OC_6H_5)_3 + Al(C_2H_5)_3$ and $Ni(acac)_2 + P(OC_6H_5)_3 + Al(C_2H_5)_3^{+} + BF_3(C_2H_5)_2O$ catalytic systems in solution in halogenohydrocarbons. The oxidative addition of the halogenohydrocarbon to the intermediate complexes results in the formation in the system of organometallic nickel complexes of the type



$$\underset{\underset{L}{\uparrow}}{R-Ni}\begin{matrix}\nearrow Hal \searrow \\ \nwarrow F \nearrow\end{matrix}M \rightleftarrows \left[\begin{matrix}RNi\\ \uparrow\\ L\end{matrix}\right]^+ [MHalF]^-$$

where M = B or Al, L = phosphorus-containing ligand, and X = halide ion.

The nature of the activating ligand influences also the composition of the codimerisation products. Chlorine-containing compounds direct the process towards the preferential formation of 4-PP-2.[27] In the presence of boron trifluoride etherate, the reaction products contain a large amount of 4-PP-1. Catalytic systems containing $Al(C_2H_5)_2Cl$ exhibit a high activity without electron-accepting additives and the isomeric composition of the phenylpentenes depends in this case on the nature of the electron-donating ligand and the P:Ni ratio. For the ratio P:Ni = 1, 2-methyl-3-phenylbut-1-ene, the product of the "tail to tail" addition (yield up to 15%), is present among the reaction products together with 4-phenylpentenes. The increase of the P:Ni ratio to 4:1 or the replacement of the phosphorus-containing ligand by bipyridyl fully suppresses the "tail to tail" addition. The main reaction product is then 4-PP-2 (95–96%). In the absence of electron-donating ligands, a large amount of styrene oligomerises, which reduces the yield of phenylpentenes.[27,29,30]

Thus the introduction of phosphorus-containing ligands into the coordination sphere of nickel increases the selectivity of the codimerisation of styrene with ethylene and propene. The most active catalytic centres contain electron-accepting acido-ligands and neutral ligands. The nature of the acido-ligand in the initial nickel compound has a significant influence on the activity and selectivity of the action of nickel-containing systems of the type of Ziegler–Natta catalysts, which indicates the retention of the bond between this ligand and nickel in the catalytic centres. This is also indicated by the results of kinetic studies.[8,24,27,29,30-33]

IV. GENERAL KINETIC FEATURES OF THE STYRENE OLIGOMERISATION AND CO-OLIGOMERISATION REACTIONS

The orders of the oligomerisation and co-oligomerisation with respect to the monomers depend on the nature of the components, the composition of the catalytic systems, and the reaction temperature. In the dimerisation of styrene in the presence of the nickel *NN*-diethyldithiocarbamate + diethylaluminium chloride two-component system, the reaction order depends on temperature and varies from 0.43 to 0.95 in the range 10–33 °C. When triphenyl phosphite is introduced into the catalyst, the reaction order with respect to styrene becomes unity and is independent of temperature but the molecular weight of the oligostyrene is then found to increase.[24]

A change in reaction order is observed also in the codimerisation reactions of styrene or α-methylstyrene with ethylene and propene.[8,28-30,33] In this case, the rates of formation of the codimers obey the complex relation $v = K[\text{catalyst}][\text{styrene}]^n[\text{olefin}]^m$, where K is the codimerisation rate constant and n and m depend on the nature and concentration of the olefin, the nature of the catalyst components, and temperature, varying in the range from 0 to 1 (Table 1). Thus, in the codimerisation of styrene with ethylene in the presence of the $Ni(acac)_2 + P(OC_6H_5)_3 + Al(C_2H_5)_3 + BF_3(C_2H_5)_2O$ catalytic system, which exhibits a moderate activity, at −30 °C the rate of formation of 3-phenylbut-1-ene is almost independent of both the initial styrene concentration and time, i.e. $n = m = 0$.[32]

Table 1. The orders of the codimerisation reactions of styrene and α-methylstyrene with ethylene.

Catalytic systems*	T, °C	Reaction order w.r.t. styrene or α-methylstyrene	 w.r.t. ethylene	Refs.
Styrene				
$Ni(acac)_2P(OC_6H_5)_3 + (C_2H_5)_3Al + BF_3\cdot(C_2H_5)_2O$, where Ni:P:Al:B = 1:1:3:5	−30 5 15 25 **	0 0.7 — 1.0	0.7 0.7 0.9 1.0	[33]
$Ni(acac)_2 + Li + (C_2H_5)_3Al + BF_3\cdot(C_2H_5)_2\cdot O$, where Ni:bipy:Al:B = 1:1:3:5	25	0	0.4	[33]
$Ni(acac)_2 + P(OC_6H_5)_3 + (C_2H_5)_2Al$, where Ni:P:Al = 1:1:100	−30 −20	0 0	— —	[33]
$Ni(DEDTC)_2 + P(OC_6H_5)_3 + (C_2H_5)_2AlCl$, where Ni:P:Al = 1:1:100	−20 −10 2 **	0 0 0	— —	[8]
$Ni(DEPDT)_2 + P(OC_6H_5)_3 + (C_2H_5)_2AlCl$, where Ni:P:Al = 1:1:100	−20 −10 2 ** 10	0 0 0 0	— — — —	[8]
α-Methylstyrene				
$Ni(DPPDT)_2 + (C_2H_5)_2AlCl$, where Ni:Al = 1:100	−10 2 10	0 0 0	— — —	[8]
$Ni(acac)_2 + P(OC_6H_5)_3 + (C_2H_5)_3Al + BF_3(C_2H_5)_2O$, where Ni:P:Al:B = 1:1:3:5	25 15 5	0.8 0 0	0.9 — 0.7	[33]

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* DEDTC = diethyldithiocarbamate, DEPDT = diethyl phosphorodithioate, DPPDT = diphenylphosphorodithioate, and bipy = bipyridyl.

** The reaction order with respect to nickel is 1.

An analogous behaviour has been observed also in the codimerisation of α-methylstyrene with ethylene at 15 °C.[33] With increase of temperature to 25 °C, there is a transition from the zero reaction order with respect to α-methylstyrene to the first order process. When phosphite in the catalyst is replaced by αα′-bipyridyl, the zero order with respect to styrene is retained also at 25 °C. The same reaction order is observed also in the presence of highly active catalytic systems containing organic dithio-derivatives of nickel (dithio-systems).[8,29,30] The reaction order with respect to ethylene likewise depends on temperature and, when the reaction order with respect to styrene (or α-methylstyrene) is zero, it is less than unity, while under the conditions where the rate of codimerisation is directly proportional to the styrene concentration the order with respect to ethylene is also unity. At a methylene pressure above 0.3 MPa, the rate of codimerisation in the presence of the dithio-systems is independent of the styrene and ethylene concentrations.[8]

In the codimerisation of styrene with propene, the reaction order with respect to propene in the range of concentrations of the latter 1–7 M is independent of the nature of the catalyst and is close to unity, while the order with respect to styrene varies from 0 to 1 (Table 2). Depending on the nature of the catalyst components, the kinetic curves can be S-shaped or can be straight lines, the latter being observed in the presence of three-component dithio-systems.[27,29,30] Linear kinetic plots imply that in the presence of these systems the rate of codimerisation does not change when the concentrations of the monomers are varied with time, i.e. in this case a zero reaction order with respect to both monomers is attained.

V. DEPENDENCE OF THE FORM OF THE KINETIC EQUATIONS FOR THE OLIGOMERISATION AND CO-OLIGOMERISATION OF STYRENE ON THE NATURE OF THE LIGANDS

A common stage in the processes involving the oligomerisation of styrene and its codimerisation with olefins is the addition of the first styrene molecule to nickel hydride. The second monomer added in oligomerisation is again styrene, while in co-dimerisation it is ethylene or propene. The dependence of the reaction order with respect to the reacting monomers on the nature of the catalyst components and the experimental conditions indicates in general the equilibrium character of the stages in which the monomers are added to the active centres and confirms the two-stage nature of

Table 2. The orders of the codimerisation reaction of styrene with propene with respect to the monomers.[29,30]

Catalytic system	T, °C	2-M-3-PB-1 n	 m	4-PP-1 n	 m	4-PP-2 n	 m	Sum of codimers n	 m
$Ni(acac)_2 + bipy + (C_2H_5)_2AlCl$	23	—	—	0	1.24	0	1.11	0	1.0
$Ni(acac)_2 + P(OC_6H_5)_3 + (C_2H_5)_2AlCl$	23	0.90	1.10	0.92	1.10	1.20	1.17	1.04	1.08
Ditto	2	1.30	0.77	1.08	1.14	0.89	1.11	1.00	0.82
$Ni(acac)_2 + P(OC_6H_5)_3 + (C_2H_5)_2AlCl$	23	0.80	0.85	0.80	0.70	0.90	1.14	0.98	1.17
$Ni(acac)_2 + P(O{-}CH_3C_6H_4O)_3 + (C_2H_5)_2AlCl$	23	0.87	1.20	0.90	1.20	1.00	0.92	1.10	0.88
$Ni(DPPDT)_2 + P(OC_6H_5)_3 + (C_2H_5)_2AlCl$	2	—	—	0	1.07	0	1.10	0	1.10
$Ni(DEDTC)_2 + P(OC_6H_5)_3 + (C_2H_5)AlCl$	2	—	—	0	0.95	0	1.00	0	1.00
$Ni(DEDTC)_2 + P(OC_6H_5)_3 + (C_2H_5)_2AlCl$ *	2	—	—	0	1.00	0	1.06	0	1.04

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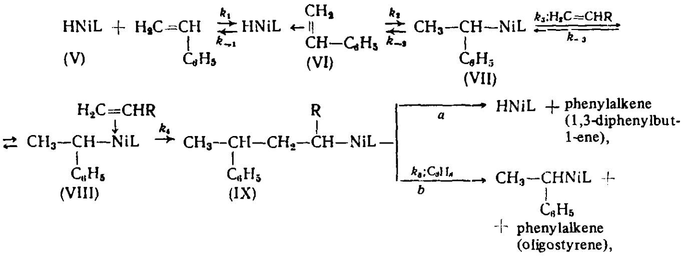
*Catalyst prepared in the presence of styrene.

this reaction (the presence of coordination and insertion stages):



where R = C_6H_5 in oligomerisation and R = H or CH_3 in codimerisation.

It has been shown[29,30,33] that the rate of codimerisation is satisfactorily described by the general kinetic equation

$$v_1 = \frac{\alpha\beta k_4 K'K''K''' [\mathrm{Ni}]_0 [\mathrm{St}]_0 p}{1 + (K' + K'K'' + \beta K'K''K''' p) [\mathrm{St}]_0} \tag{1}$$

and when the reaction order with respect to styrene is zero by the equations

$$v_1 = \frac{\alpha\beta k_4 K'K''K''' [\mathrm{Ni}]_0 p}{K' + K'K'' + \beta K'K''K''' p} \tag{2}$$

$$v_2 = \frac{\alpha\beta k_3 k_4 k_5 [\mathrm{Ni}]_0 p}{(k_{-3} + k_4) k_5 + (k_4 + k_5) \beta k_3 p} \tag{3}$$

where ν_1 and ν_2 are the rates of formation of the codimers via pathways *a* and *b* respectively, α is the fraction of active codimerisation centres relative to the initial concentration of the nickel compound, β the solubility coefficient of the olefin, k_3, k_{-3}, k_4, k_{-4}, and k_5 are the rate constants for the corresponding elementary stages, K', K'', and K''' the stability constants of the complexes (VI), (VII), and (VIII) respectively, p is the olefin pressure, and $[\mathrm{Ni}]_0$ and $[\mathrm{St}]_0$ are the initial concentrations of the nickel compound and styrene respectively.

For zero order with respect to both reacting monomers, the rate of codimerisation via pathway *b* obeys the equation[8]

$$v_2 = \frac{\alpha k_4 k_5 [\mathrm{Ni}]_0}{k_4 + k_5} \tag{4}$$

or, when $k_5 \geq k_4$, the equation

$$v_2 = \alpha k_4 [\mathrm{Ni}]_0 \tag{5}$$

When the reaction order with respect to styrene is zero and that with respect to olefins is unity, we have

$$v_1 = \frac{\alpha\beta k_4 K'K''K''' [\mathrm{Ni}]_0 p}{K' + K'K''} \tag{6}$$

$$v_2 = \frac{\alpha\beta k_3 k_4}{k_{-3} + k_4} [\mathrm{Ni}]_0 p \tag{7}$$

If $k_{-3} \gg k_4$, then according to Eqn.(7) the effective codimerisation rate constant $k_{\mathrm{eff}} = \alpha\beta k_4 K'''$, i.e. it depends both on the stability constant K''' and on the rate constant k_4 for the insertion stage. If the temperature coefficient of the constant K''' is then low, the activation energy for the overall codimerisation process is determined mainly by the activation energy for the insertion stage. On the other hand, if $k_{-3} \ll k_4$, then $k_{\mathrm{eff}} = \alpha\beta k_3$ and the activation energy is determined by the temperature dependence of the rate constant for the complex formation stage. Usually $k_{-3} \gg k_4$ in the codimerisation of styrene with ethylene and propene,[8,29,30,33] while in the oligomerisation of styrene we have the opposite situation with $k_{-3} \ll k_4$.[27-29] Consequently the first order of the oligomerisation reaction is a consequence of an appreciable contribution by the complex formation step in the propagation stage to the overall process kinetics. The effective rate constant for chain propagation in then identical with the complex formation rate constant.[8] The experimental results are described satisfactorily by the equation[24]

$$v_{\mathrm{d}} = \frac{\alpha k_1^* k_2^* k_3^* [\mathrm{Ni}]_0 [\mathrm{St}]_0}{k_3^* (k_1^* + k_2^*) + k_1^* k_2^* [\mathrm{St}]_0} \tag{8}$$

$$v_{\mathrm{ol}} = \alpha(k_p^* + k_t^*)[\mathrm{Ni}]_0[\mathrm{St}]_0, \tag{9}$$

$$\overline{P}_{\mathrm{p}} = \frac{k_p^*}{k_t^*} + 1, \tag{10}$$

where ν_{d} and ν_{ol} are the rates of dimerisation and oligomerisation of styrene respectively, $\overline{P}_{\mathrm{p}}$ is the average degree of polymerisation of styrene, k_1^* and k_2^* are the effective rate constants for the stages involving the addition of the first and second molecules of styrene in dimerisation, k_3^* is the effective rate constant for the elimination of the dimerisation product (1,3-diphenylbut-1-ene) from the complex (IX), and k_p^* and k_t^* are the effective rate constant for chain propagation and chain transfer to the monomer in the oligomerisation of styrene. The remaining notation was explained above.

VI. KINETIC PARAMETERS OF THE ELEMENTARY STAGES IN THE STYRENE OLIGOMERISATION AND CO-OLIGOMERISATION PROCESSES

Eqns.(1)–(10) and their forms in terms of the variables $1/\nu_i$ and $1/[\mathrm{M}]$, where ν_i is the rate of formation of the *i*th produce and [M] the concentration of one of the reacting monomers, make it possible to determine the rate constants for the elementary stages or their combinations and to estimate how they vary as a function of the nature of the components and the composition and conditions governing the preparation of the catalyst.

The kinetic parameters of the dimerisation and oligomerisation of styrene calculated with the aid of Eqns.(1)–(3) have been published.[24] The introduction of a phosphorus-containing ligand into the catalyst increases the activation energy for chain propagation (39 kJ mol^{-1} in the two-component system and 58–63 kJ mol^{-1} in the three-component system). At the same time, as shown above, the character of the chain termination changes on passing from dimerisation to oligomerisation: instead of the β-elimination of nickel hydride, chain transfer to the monomer takes place. The activation energy for chain termination then changes little but the ratio of the chain propagation and chain termination rate constants increases, which ultimately promotes the formation of an oligomer with a high molecular weight.[24]

Phosphorus-containing ligands exert the opposite influence on the activation energy for the codimerisation of styrene with ethylene.[8,28] On passing from the two-component to the three-component system, the activation energy for codimerisation falls sharply (almost by a factor of two), while the rate constant increases by a factor greater than 10.

The kinetic parameters change also in the codimerisation of styrene with propene:[29,30] depending on the nature of the catalyst components, the activation energy E_a ranges from 29–33 to 63–64 kJ mol^{-1}. It decreases on passing from the two-component to the three-component system and from the acetylacetonate system to the dithio-system. The activation energy for the formation of 4-PP-2 is in all cases greater than that for the formation of 4-PP-1 (by 8–16 kJ mol^{-1}). However, the rate of formation of 4-PP-2 is higher than the rate of formation of 4-PP-1 even along the initial sections of the kinetic curves, where the degree of isomerisation of 4-PP-1 to 4-PP-2 is very low.[27,29,30,34] Hence it follows that at least in the initial instant 4-PP-1 and 4-PP-2 are formed on different centres, the centres for the formation of the second isomer predominating.

The opposite influence of phosphorus-containing ligands on the activation energies for styrene oligomerisation and codimerisation processes is a direct consequence of the different nature of the rate-limiting stages in these processes. The presence of a phosphorus-containing ligand in the coordination sphere of nickel diminishes the activation energy for the insertion stage and increases that for the olefin coordination stage.

Table 3. Kinetic parameters of the polymerisation of butadiene.[1,35,37,38]

Catalytic system	T, °C	N_p, %	k_p, litre mol^{-1} min^{-1}	k_d, litre mol^{-1} min^{-1}	Activation energy***, kJ mol^{-1}	
					E_p	E_d
$(C_4H_7NiCl)_2$ – dichloroquinone	20	7	11	44	33.4	20.6
	30	7	18	58		
	50	8	40	98		
$(C_4H_7NiCl)_2$ – chloranil*	0	10	12	30	26.0	15.7
	10	9	20	36		
	20	9	27	50		
	30	8.5	46	63		
	40	—	58	73		
$(C_4H_7NiCl)_2$ — fluoranil	7	16	32	46	30.0	17.0
	20	17	49	67		
	30	17	85	82		
C_5H_9NiCl + chloranil	22	—	153	80	—	—
$[(C_2H_5O)_2PS_2]_2Ni$ + $(C_2H_5)_2AlCl$ **	15	44	437	349	30.5	49.7
	25	36	898	1076		
	35	28	967	1376		
	45	20	1415	3028		

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* The rate constants for the chain transfer to the monomer (k_t^M/k_p) and to the catalyst (k_{cat}/k_p) at 25 °C are $k_t^M/k_p = 2 \times 10^{-4}$ and $k_{cat}/k_p = 5 \times 10^{-3}$.

** $k_t^M/k_p = 1.3 \times 10^{-2}$ and $k_{cat}/k_p = 1.1 \times 10^{-2}$.

*** The activation energy for the polymerisation of butadiene in the presence of pure π-alkenylnickel is 60–70 kJ mol^{-1},[1] while in the presence of the $[(C_2H_5O)_2PS_2]_2Ni$ + bipyridyl + $(C_2H_5)_2AlCl$ catalytic system it amounts to 56.2 kJ mol^{-1}.[37]

VII. KINETIC PARAMETERS OF THE ELEMENTARY STAGES OF THE POLYMERISATION OF BUTADIENE

The dependence of the kinetic parameters of the elementary stages of the process on the nature of the ligands can be traced in relation to the polymerisation of butadiene in the presence of catalytic systems of three different types: π-alkenylnickel chloride + quinones,[35,36] nickel *NN*-diethyldithiocarbamate + diethylaluminium chloride, and nickel *NN*-diethyldithiocarbamate + diethylaluminium chloride + bipyridyl.[37,38] The kinetic constants were calculated from the rates and degrees of polymerisation with the aid of the corresponding kinetic equations. The initial concentrations of the chain propagation centres in the π-alkenyl systems were estimated from the initial concentration of the growing chains.[36] The standard deviation of the calculated values of the parameters listed in Table 3 from the experimental values was less than 3%.

Table 3 shows that the concentration of the propagation centres N_p is in all systems less than the initial concentration of the nickel compound, amounting to not more than 44% of $[Ni]_0$ depending on the nature of the catalyst components and the experimental conditions. In the case of the dithio-system, the calculated maximum concentration of the propagation centres diminishes with increase of temperature, which is due to their bimolecular deactivation.[37,38] The activation energy for the destruction of the centres E_d in this system exceeds that for the chain propagation E_p by ~18 kJ mol^{-1}. In the presence of an electron-donating ligand (bipyridyl), a sharp increase of the process activation energy is observed.[37]

The introduction of electron-accepting ligands (quinones) into π-alkenyl systems tends to decrease the activation energy for polymerisation.[1] Both the propagation rate constants k_p and the bimolecular deactivation rate constants k_d increase on passing from a weaker π-electron acceptor (dichloroquinone) to a stronger acceptor (chloranil, fluoranil), while the corresponding activation energy diminishes under these conditions.

The stronger activating effect of fluoranil (compared with chloranil) is a consequence of the increased concentration of the propagation centres and the high activation energy for chain propagation (25–30 kJ mol^{-1}), while the difference between the electron affinities of these quinones is small (the half-wave potentials for chloranil and fluoranil are respectively +0.01 and −0.04 V).[35,36]

The presence in the catalyst of a strongly nephelauxetic dithio-ligand[39] increases appreciably (by two orders of magnitude and above) the rate constants for the elementary stages compared with powerful π-electron acceptors such as halogenoquinones. However, this increase is achieved by virtue of the more favourable steric conditions and not as a result of the decrease of the activation energy, because the E_a in the highly active dithio-system either differs little from the E_a in the π-alkenylnickel chloride + quinone systems or exceeds it (cf. E_p and E_d in Table 3).

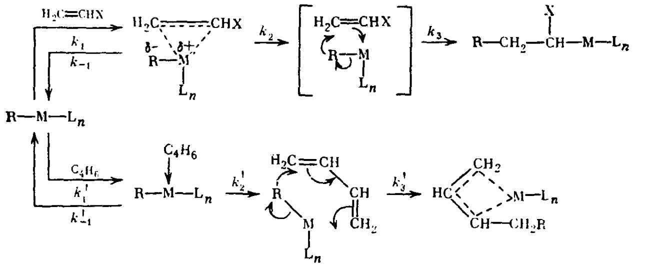
As for the π-alkenyl systems, one of the principal chain termination reactions in the presence of dithio-systems is chain transfer to the monomer. However, the rate constant for this last stage in the presence of dithio-systems is higher by two orders of magnitude, which causes the formation of low-molecular-weight polybutadiene,[37] while the less active π-alkenyl systems lead to the formation of high-molecular-weight polybutadiene.[1]

Thus, in the polymerisation of butadiene electron-accepting ligands diminish the activation energy for the chain propagation stage, while electron-donating ligands increase it. The molecular weight is determined not so much by the steric characteristics of the ligands as by their energetic (electronic) characteristics.

VIII. THE S_ECi MECHANISMS OF THE CATALYTIC ACTION OF NICKEL-CONTAINING SYSTEMS. THE ROLE OF ELECTRONIC AND STERIC PROPERTIES OF THE LIGANDS

The study of the influence of various electron-donating and electron-accepting ligands on the activity and selectivity of nickel-containing systems in dimerisation, codimerisation, oligodimerisation, and polymerisation processes and also on the kinetic parameters of these reactions has shown that electron-accepting ligands as a rule tend to decrease the activation energy and to increase the rate of the process. The influence of electron-donating ligands in various reactions is manifested in different ways: they increase the activation energies for the oligomerisation of styrene and the polymerisation of butadiene, while they decrease the activation energy for the codimerisation of styrene with ethylene and propene.

The results obtained make it possible to regard the elementary stage involving the addition of the monomer to the catalytic hydride or organometallic centre as an electrophilic reaction proceeding via a stage in which the monomer undergoes nucleophilic coordination to the metal (Abraham's S_ECi mechanism):[9]



where R = H, alkyl, benzyl, or alkenyl and L_n = set of remaining ligands.

This approach makes it possible to classify the catalytic mechanisms of nickel-containing systems in linear oligomerisation and polymerisation processes in terms of the kinetic features of the reactions and the electronic effects of the ligands from a single standpoint and to explain the causes of the opposite influence of the introduction of phosphorus-containing ligands on the activation energies for various processes.

According to these ideas, in those cases where the rate-limiting stage is the nucleophilic coordination of the monomer to the metal, the introduction of an electron-donating ligand into the coordination sphere of nickel increases the activation energy for the process. On the other hand, if the electrophilic insertion of a coordinated monomer molecule becomes the rate-limiting stage, then electron-donating ligands tend to decrease the activation energy, apparently as a consequence of the increase under their influence of the electron density at the α-carbon atom in the Ni–C bond. The activation of the system reacting via the first mechanism takes place under the influence of electron-accepting ligands, while the prescence of electron-donating ligands is essential for the activation of systems reacting via the second mechanism. The first type of activation is manifested in styrene oligomerisation reactions[31,32] and also in the polymerisation of butadiene.[1,40–42] The codimerisation reactions of styrene with ethylene and propene are examples of activation of the second type.[8,29,30]

The styrene oligomerisation and co-oligomerisation reactions then proceed via different versions of the S_ECi mechanism, which differ by the nature of the rate-limiting stages and correspondingly by the overall orders with respect to the reactants.

Investigations have shown that the overall kinetic features of the dimerisation, oligomerisation, and polymerisation reactions in the presence of nickel-containing systems vary within wide limits, so that the rates of the overall processes can be described by first-, second-, third-, and fractional-order kinetic equations.[8,24,29,30,33,35,36] In terms of the S_ECi mechanism, the corresponding versions can be classified as the S_E1Ci, S_E2Ci, S_E3Ci, and S_EnCi mechanisms.

Such mechanisms obtain when the nucleophilic coordination of the monomer is a rapid non-equilibrium process and the kinetics of the overall reaction is determined by the electrophilic insertion stage. The effective rate constant is then identical with the overall rate constant for the insertion process. A characteristic feature of the S_E1Ci mechanism is the independence of the rate of the process of the concentrations of the reacting monomers. The activation of systems acting via the S_E1Ci mechanism is possible when electron-donating ligands, increasing the heteropolar character of the $R^{\delta -}–M^{\delta +}$ bond, are introduced into the coordination sphere of the metal. This is achieved by reducing the activation energy for the insertion stage. Examples of the S_E1Ci mechanism are provided by the codimerisation reactions of styrene with ethylene and propene in the presence of dithiosystems.

The S_E2Ci mechanism is determined by the contribution of the nucleophilic coordination of the monomer to the overall process kinetics, whereupon the effective rate constant is either equal to the complex formation rate constant ($k_{eff} = k_1$) or represents a combination of the rate constants for elementary stages (for example, $k_{eff} = k_1k_2/k_{-1}$, where k_2 is the overall rate constant for the insertion stage). When the equality $k_{eff} = k_1$ holds, the process activation energy increases in the presence of electron-donating ligands, which diminish the effective positive charge on the metal and thereby retard the nucleophilic monomer coordination stage, which determines the overall rate of reaction. In order to increase the efficiency of the catalytic action of the system, it is essential to introduce electron-accepting, neutral and nephelauxetic acido-ligands into the coordination sphere of the metal. The introduction of these ligands increases the effective positive charge on the metal as a result of the formation of inner-sphere π-bonds or bridging σ-bonds (M...X...L) and also anisotropic or outer-sphere complexes with transfer of charge (and the anion), which ultimately diminishes the process activation energy. Such influence of the ligand is characteristic of styrene oligomerisation and butadiene polymerisation processes. If $k_{eff} = k_1k_2/k_{-1}$, then the introduction of electron-donating ligands into the coordination sphere of the metal decreases the process activation energy, because the stage involving the electrophilic insertion of the coordinated monomer molecule becomes rate-determining. This version of the S_E2Ci mechanism operates in the codimerisation of styrene with ethylene and propene in the presence of acetylacetonate systems. Apart from the first order with respect to the monomer, its characteristic feature is the decrease of the process activation energy after the introduction of electron-donating ligands into the catalyst.[29,30,33]

The S_E3Ci mechanism is manifested when the effective rate constant for the process includes the rate constants (or equilibrium constants) for the nucleophilic stages in which two molecules of the same monomer or the molecule of different monomers are coordinated (for example, $k_{eff} = K'K''k_2$, where K' and K'' are the stability constants of the π-complexes incorporating one and two molecules of identical or different monomers respectively and k_2 is the insertion rate constant). The addition of two molecules can take place either consecutively or simultaneously, while the insertion of one molecule is accompanied by the reversible coordination of another. The principal distinctive feature of this mechanism is the overall second order with respect to the reacting monomers (monomer) and the first order with respect to the catalyst. The influence of electron-donating and electron-accepting molecules on the process activation energy is the same as in the S_E2Ci mechanism. This case obtains in the codimerisation of styrene with ethylene and propene in the presence of acetylacetonate systems at elevated temperatures (>15 °C). It apparently occurs also in many other instances of the homo- and co-oligomerisation of olefins and also in polymerisation under the influence of metal complex systems when the overall order with respect to the monomer is two.[1,4]

The S_EnCi mechanism occupies an intermediate position between the S_E1Ci and S_E2Ci mechanisms or between the S_E2Ci and S_E3Ci mechanisms. It obtains when the contributions of the nucleophilic and electrophilic components in the S_ECi addition are comparable. The effective process rate constant is a complex combination of rate constants and at least one of the terms in the denominator of the rate equation includes the monomer concentration [for example, Eqns. (1), (2), and (8)]. A characteristic feature of this mechanism is the fractional overall order with respect to the monomers ($1 < n < 2$ or $2 < n < 3$). The temperature dependence of the reaction orders with respect to the monomers must be regarded as a second characteristic feature. The activating influence of the ligands on the properties of catalytic systems is in this case indefinite. It depends on the ratio of the rate constants for the nucleophilic and electrophilic stages in the S_ECi addition. In particular, electron-donating ligands can both decrease and increase the process activation energy or they may not influence it at all. The S_EnCi mechanism is apparently encountered more often than the other mechanisms. It can be clearly traced in the styrene dimerisation reactions and in the codimerisation of styrene with ethylene and propene and is apparently also observed in diene polymerisation reactions.[1,8,24,29,30]

The proposed classification of the mechanisms of catalytic action make it possible to make sense of the wide variety of kinetic features observed in the linear oligomerisation and polymerisation processes catalysed by nickel-containing and other systems. It helps in many respects to predict the mechanisms of the activating action of ligands and to understand the causes of opposing influences on the catalytic efficiency of systems in various ologomerisation and polymerisation reactions. The influence of polar solvents on the rate of catalytic processes can be satisfactorily explained from the standpoint of the S_ECi mechanisms: highly basic solvents (ethers, sulphides, amines) hinder the nucleophilic coordination of the monomer, competing with the latter for the inner coordination sphere of the metal, while halogenohydrocarbons, capable of forming anisotropic or outer-sphere charge-transfer complexes, accelerate it. This leads ultimately to an increase in the rate of the process, which has been demonstrated for the codimerisation of styrene with ethylene.[8]

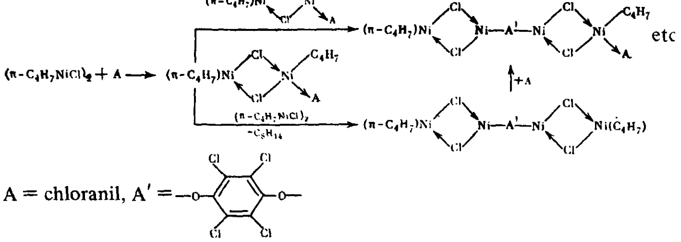
The changes, not only in the rate of polymerisation of butadiene, but also in the stereospecificity of the catalytic action of the systems under the influence of electron-donating and electron-accepting additives can be explained in terms of the S_ECi mechanisms. In the presence of electron-donating ligands in the coordination sphere of the metal, the rate of the nucleophilic coordination of the monomer is diminished, on the one hand, and the probability of such coordination of the penultimate unit, which fixes the terminal unit in the *anti*-configuration, decreases, on the other hand. The $\pi-\sigma$ and *anti–syn* isomerisation processes in the terminal unit are then facilitated, which is also promoted by the increase of the heteropolar character of the $M^{\delta+}-C^{\delta-}$ bond. As a result, the polymer microstructure shifts towards the 1,4-*trans*-configuration of the units. On the other hand, in the presence of electron-accepting ligands, both the rate of the nucleophilic coordination of the monomer and the probability of the fixation of the terminal unit in the *anti*-configuration as a result of the nucleophilic coordination of the penultimate unit increase, which leads to the 1,4-*cis*-structure of the polymer. The fact that in certain cases the influence of electron-donating ligands on the microstructure of polybutadiene, obtained in the presence of nickel-containing systems, resembles their influence in anionic systems is also striking in this respect: in both cases the content of 1,2-units increases. Thus it has been established[43–55] that the addition of triphenylphosphine to the nickel acetylacetonate + diethylaluminium chloride system with the ratios Ni : Al : P = 1 : 10 : 4 ensures the formation of polybutadiene containing 49% of the *cis*-units, 11% of the *trans*-units, and 40% of the 1,2-units.

However, one should note that this approach cannot explain all the features of the influence of ligands on the catalytic properties of the systems. In the S_ECi mechanisms, account is taken only of the influence of electronic factors from the standpoint of nucleophilic coordination and electrophilic insertion. Evidently, many oligomerisation reactions, proceeding via oxidation-reduction stages, cannot be treated, in principle, in terms of the S_ECi mechanisms. They include the majority of cyclic oligomerisation and co-oligomerisation reactions and certain linear oligomerisation reactions,[5] the key stages of which are oxidative addition (including those which lead to the formation of metallocycles) and reductive elimination. The catalysis mechanisms of these reactions constitute a special class and they are probably best referred to as redox mechanisms.

The steric effects of the ligands, which frequently play a decisive role in the overall catalytic action of the system, remain outside the range of phenomena which can be explained by the S_ECi mechanisms. These effects influence the mode of addition of the monomers, the process selectivity, the absolute rate constants for the elementary stages, and their ratios.

Ligands also have different effects on the number of catalytic centres. It has been established for the π-alkenylnickel chloride + quinone systems[41] that electron-accepting ligands diminish appreciably the concentration of such centres (4–10% of the concentration of the initial nickel compound). This conclusion was subsequently confirmed by a number of studies on the polymerisation of butadiene in the presence of catalytic systems based on π-alkenylnickel derivatives.[1]

It has been shown[42] that the interaction of π-alkenylnickel halides with electron acceptors (quinones) involves an oxidation-reduction polycomplex formation reaction leading to the formation of oligomeric and polymeric complexes with terminal alkenylmetal and metal hydride fragments containing electron-acceptor molecules bound in complexes. The formation of catalytic centres is accompanied by the formation of the products of the dimerisation of the alkenyl groups, which indicates the homolytic destabilisation of the Ni–C bond under the influence of electron-accepting ligands. The overall polycomplex formation scheme for the interaction of bis-π-crotylnickel chloride with chloranil is as follows:†



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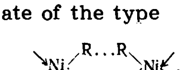
† Other possible reactions occurring in the polycomplex formation process have been considered by Azizov.[42]

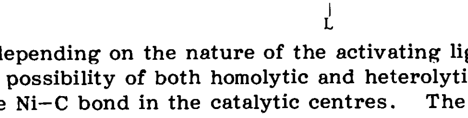
It has been suggested that the polycomplex grows via an intermediate cyclic state of the type



whose cleavage leads to the formation of the dimerisation products C_8H_{14} and the addition of a new unit to the growing end of the polycomplex. Mainly the terminal nickel atoms, constituting only a small fraction of the total number of nickel atoms, participate in the initiation of polymerisation. A low concentration of propagation centres obtains also in two-component systems of the Ziegler–Natta type, which has been established for the system based on organic dithio-derivatives of nickel and diethylaluminium chloride—10–40% of $[Na]_0$ depending on the reaction temperature.[37,40]

Electron-donating ligands exert opposite influences on the number of catalytic centres and the activation of the Ni–C bond. The increase of the effective propagation rate constant (αk_p) and the overall oligomerisation rate constant in the presence of a phosphorus-containing ligand, which is inconsistent with the increase of the activation energy for chain propagation, is striking.[24] This finding has been explained by the increase of the number of catalytic centres (or α) owing to their stabilisation as a result of complex formation with phosphorus-containing ligands. Such increase predominates over the decrease of k_p, which ultimately entails the growth of αk_p and of the overall rate of oligomerisation.

The conditions in the formation of the catalyst and the nature of the acido-ligand in the initial nickel compound also exert an appreciable influence on the number of catalytic centres in the system and hence on the effective codimerisation rate constant.[8] The preliminary formation of a three-component dithio-system in the presence of styrene entails a significant increase of the effective codimerisation rate constant.[8,28] On the other hand, the conditions governing the formation of the three-component acetylacetonate system do not exert an appreciable influence on this quantity. The activation energy depends little on the nature of the acido-ligand and on the catalyst formation conditions, but these factors do influence the pre-exponential factor, which reflects indirectly the changes in the concentration of the active centres in the system. Analysis of the changes in the pre-exponential factor in three-component systems, characterised by identical general kinetic features of the codimerisation reaction, permit the conclusion that the concentration of the active centres increases on passing from diethylphosphorodithioate to diethyl dithiocarbamate and when the catalyst is formed beforehand. The results of spectroscopic, cryoscopic, and kinetic measurements[8] have shown that this difference between the dithio-system and the acetylacetonate system is due to the slowness of the complex formation reaction between the dithio-derivative of nickel and the phosphorus-containing ligand, which takes place only after the interaction of the nickel compound with alkylaluminium halide:

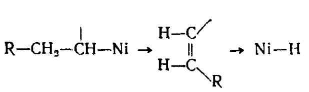


Thus, depending on the nature of the activating ligands, there is a possibility of both homolytic and heterolytic activation of the Ni–C bond in the catalytic centres. The former takes place under the influence of electron-accepting ligands, which is indicated, in particular, by the isolation of the products of the "quasi-radical" dimerisation of the alkenyl group in the reactions of π-alkenylnickel halides with electron-accepting compounds. The heterolytic activation of the Ni–C bond occurs under the influence of electron-donating ligands, which tends to decrease the activation energy for the insertion stage in the codimerisation of styrene with ethylene[8,28] and propene[29] and to increase the fraction of 1,2-units in the polymerisation of butadiene.[43–55]

The heterolytic activation of the metal–carbon bond is in certain cases apparently so great that the organometallic derivative of the transition metal becomes a catalyst of the anionic polymerisation of polar monomers, as happens, for example, in the polymerisation of methyl methacrylate in the presence of tris-π-allylchromium or the $Cr(acac)_3$–Al(isobutyl) system in combination with electron donors and also in the presence of complex catalytic systems based on vanadium and chromium compounds.[56] An analogous behaviour has been observed in the polymerisation of polar vinyl monomers under the influence of bipyridyl complexes of iron(II) and cobalt(I), having the d^6 and d^8 electronic configurations respectively.[57,58]

Homolytic activation is the main cause of the bimolecular destruction of active centres, occurring in the polymerisation of butadiene in the presence of the π-alkenyl halide + quinones[41] and nickel *NN*-diethyldithiocarbamate + diethylaluminium chloride[40] catalytic system. However, overall, the stability of the catalytic action of the system depends not only on the nature of the activating ligand but also on the type of reaction catalysed. Thus the nickel *NN*-diethyldithiocarbamate + diethylaluminium chloride system, which propagates the polymerisation of butadiene in an unstable manner (the active centres are destroyed as a function of time[40]), proved to be entirely stable in styrene oligomerisation and codimerisation processes.[8,24,34] In our view, the stability of the action of the system is determined not so much by the thermodynamic stability as by the kinetic stability of the Ni–C bond in the intermediate organometallic centres, which is reflected in the frequency of the transitions: potential centre → actual centre and actual centre → potential centre. The hydride or organometallic derivatives of nickel are then regarded as the potential centres, while the actual centres are only its organometallic derivatives.

The intensity of these transitions depend on the ease of σ,π-isomerisation[59] in the intermediate organometallic derivatives of nickel. In principle, the isomerisation can proceed without a thermal effect or with only a small positive thermal effect. This is indicated by the comparison of the energies[2,60–62] and the bonds ruptured and newly formed in the reaction:



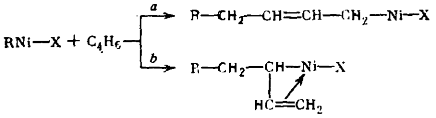
Bond	Ni—C	Ni—H	C—C	C=C	C—H	$\begin{matrix}HC\\ \Vert\\ HC\end{matrix}\to M$
Energy, kJ mol^{-1}	251	293	251	427	365	63—101

The intensity of the above transitions is therefore fairly high in the dimerisation, codimerisation, and oligomerisation processes in which intermediate alkylnickel derivatives are formed. There is insufficient time for the destruction of the catalytic centres via a bimolecular mechanism in any of the intermediate forms and the system proves to be stable. The transition: actual centre (growing chain) → potential centre (hydride or alkenyl derivative of nickel) in the polymerisation of butadiene is a slow reaction, which entails the possibility of a bimolecular destruction of the growing chains.

The intensity of the above transitions, which are in essence chain termination processes, determines also the molecular weight of the oligomerisation and polymerisation products. Among these transitions, hydrogen transfer, which proceeds with or without the elimination of a hydride complex from the intermediate organometallic derivatives of nickel has special importance. The transfer with elimination occurs, as stated above, in dimerisation and codimerisation reactions and that without elimination takes place in oligomerisation and polymerisation processes. The ease of hydrogen transfer depends on the degree of σ,π hyperconjugation between the *d* orbitals of the metal atom and the σ bonding orbitals of the β-C–H bond.[2,63] Therefore all the factors leading to a decrease of the degree of σ,π conjugation (increase of the multiplicity of the bonding of the organic group to nickel in the sequence σ-alkyl < π-benzyl < π-alkenyl, the presence of bulky ligands in the coordination sphere of the metal, decrease of temperature, stereochemical factors) in the intermediate complexes can promote an increase of the molecular weight of the reaction products. The fact that the introduction of both electron-donating (tertiary phosphines, phosphites[24]) and electron-accepting (metal trichloroacetates[20-22]) ligands into the catalyst increases the molecular weight of oligostyrene, although it has different effects on the activation energy for the overall process, is important in this respect. Consequently, the molecular weight of the oligomerisation products depends primarily on the steric effects of the ligands and not on their electronic effects.

An analogous picture has been observed also in the polymerisation of butadiene; the less active π-alkenylnickel chloride + halogenoquinones systems ensure the formation of high-molecular-weight polybutadiene,[35,40,64] while the highly active catalysts based on organic dithio-derivatives of nickel lead to the formation of only low-molecular-weight products.[37,40] Analysis of the results of kinetic measurements[35,38] has shown that the former systems are sterically less favourable at the chain termination stage involving transfer to the monomer or the transfer of a β-hydrogen atom. In the latter systems, the transfer to the monomer is a hundred times and more faster (Table 3).

It is noteworthy that in the absence from the monomer of a β-hydrogen atom which can be readily split off, the polymerisation process in the presence of nickel systems can proceed via the mechanism of "living" chains. Thus the polymerisation of 1,1-dimethylallene in the presence of bis-π-allylnickel bromide takes place via this mechanism.[65] The "living" chains mechanism is observed also in the early stages of the 1,4-polymerisation of butadiene in the presence of π-alkenyl systems,[1,36,41,66] which has also been explained by the absence of a β-hydrogen atom capable of being readily split off from the growing alkenylnickel derivative formed on 1,4-dissociation of the double bonds of butadiene (pathway *a*):



It is therefore entirely possible that chain termination in the polymerisation of butadiene in the presence of nickel-containing systems via hydrogen transfer mechanisms takes place mainly as a result of 1,2-dissociation of the double bond (pathway *b*). The relation between the molecular weight and the microstructure of polybutadiene synthesised in the presence of *cis*-directing systems may serve, in our view, as important evidence in support of this hypothesis.[67] The relation is explained by the fact that the processes concerned with the regulation of both the molecular weight and the microstructure involve the formation of the same intermediate σ-complex (via pathway *b*), in which there is a possibility of interaction between the β-C–H bond and nickel.

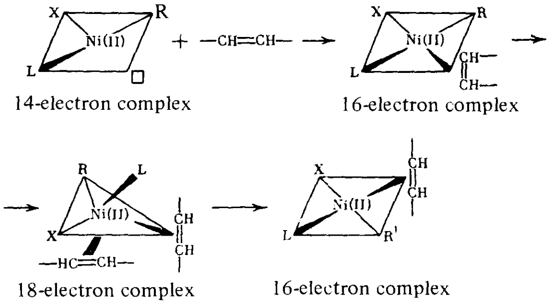
The results of a study,[68] in which the possibility of the polymerisation of butadiene via the "living" chain mechanism up to high degrees of conversion of the monomer in the presence of the bis-π-allylnickel trifluoroacetate + triphenylphosphine or chloranil catalytic system has been established, constitute convincing confirmation of the above considerations. In the polymerisation in heptane at 55 °C (with the ratio P/Ni = 0.18), a linear relation is observed between the number-average molecular weight and the degree of conversion and a satisfactory correlation between the experimental and calculated degree of polymerisation. After the exhaustion of the first and the addition of new portions of the monomer, polymerisation continues and there is a further increase of $\bar{M}_n$. It must be specially emphasised that the content of 1,4-units in the polymer investigated reaches 99% and above and also the fact that the increase of the molecular weight is promoted by both electron-donating (triphenyl phosphite) and electron-accepting (chloranil) ligands.

The conclusion that steric factors play a decisive role provides a key to the understanding of the principles governing the regulation of the structures and molecular weights of the products of the oligomerisation and polymerisation of unsaturated hydrocarbons in the presence of obtaining higher olefins and polyethylene from ethylene in the presence of these systems,[69-73] which had been previously thought to be unsuitable for these processes.

Steric effects influence also the selectivity of the codimerisation reactions of styrene with ethylene and propene. As shown above, on passing from a three-component to a two-component system, the selectivity of the codimerisation with respect to be ethylene (propene) which has reacted falls. Consequently, in the addition of the second monomer molecule to the active centres, steric hindrance in the coordination and insertion stages plays the main role and not the stabilisation energy of the newly formed Ni–C bond (which decreases in the sequence π-benzyl > σ-alkyl). In the presence of bulky phosphorus-containing ligands, the coordination of styrene is greatly hindered, as a result of which the ethylene (propene) molecule adds exclusively (or preferentially) to the intermediate benzyl derivative. In the absence of such ligands, the probability of the addition of the second styrene molecule increases and this lowers the selectivity of the codimerisation with respect to the styrene which has reacted.[8,24,27,29,30]

The opposite picture is observed in the addition of the first monomer molecule to hydride centres. As shown above, in the absence of phosphorus-containing ligands, the selectivity of the codimerisation with respect to the ethylene which has reacted, amounts to only 18%.[8,24] The remaining ethylene is converted into butenes, which means that ethylene and not styrene adds to a considerable proportion of the hydride centres. On the other hand, in the presence of phosphorus-containing ligands, styrene adds to them preferentially. The selectivity of the codimerisation with respect to the ethylene which has reacted then reaches 90–95%.[8,24] These results are also explained by the decrease of the probability of β-elimination from the benzyl derivative of nickel in the presence of phosphorus-containing ligands, hindering the σ,π-interaction, in the coordination sphere. Thus the steric effect of the ligands regulates not only the molecular weights but also the structures of the oligomerisation and polymerisation products.

However, one should note that, whereas the influence of electronic factors can be readily explained qualitatively from the standpoint of the S_ECi mechanism, this cannot be said of the steric factors. The latter apparently influence the geometry of the catalytic complexes, which in fact determines the very possibility of the catalytic process. In the dimerisation and oligomerisation reactions catalysed by transition metal complexes, there may be transitions between 14-, 16-, and 18-electron complexes.[74,75] For nickel, the 18-electron complexes are less stable than the 16-electron complexes. Therefore, if the initial centre is a 16-electron organometallic or hydride complex, the coordination of the first monomer molecule can be completed by its insertion in the Ni–C or Ni–H bond. If, on the other hand, the coordination of one monomer molecule results merely in building up the coordination sphere of the metal with formation of a stable 16-electron square-planar complex, then insertion requires the coordination of a second monomer molecule. This results in the formation of a less stable pentacoordinate 18-electron nickel complex, which readily isomerises to the tetracoordinate 16-electron complex in the insertion process:

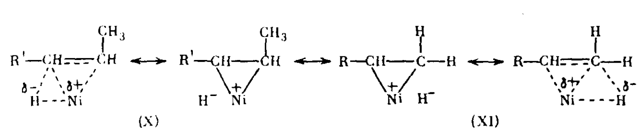


There is at present no information about the geometry of the active centres and it is therefore difficult to judge which of the geometrical dispositions is energetically most favourable. However, presumably the very possibility of the control of the sequence of the addition of monomers is determined primarily by the geometry of the intermediate states. The question of the monomer coordination and insertion sites is important in this respect. The few available experimental data show that, of the two mechanisms of the addition of olefins at the C–metal bond (*cis*-migration or insertion), *cis*-migration is preferred.[76] Evidently, in this case, for a specific disposition of the initial ligands, after each insertion stage three coordination sites appear alternately in the *cis*- and *trans*-positions relative to the ligand L. In relation to the organic group (or the α-carbon atom), the vacancy is always found to be in the *cis*-position.

The influence of the ligands on the selectivity of the codimerisation is probably determined by the different accessibilities of the *cis*- and *trans*-positions with respect to the ligand L in the coordination of monomers. In the codimerisation of styrene with ethylene (propene), ethylene (propene) is more readily coordinated in the *cis*-position in the intermediate benzyl derivative, while in the sterically less hindered *trans*-position in the initial hydride complex, the coordination of styrene is more favourable. The d_π, π_π interaction between the non-bonding *d* orbitals of the metal and the π orbitals of the benzene ring is then facilitated, which yields an additional energy gain. In the case of the sterically less favourable derivative of L having *cis*-vacancies, the d_π, π_π interaction is insignificant owing to the shielding of the non-bonding *d* orbitals of nickel by the bulky groups of the ligand L. Such alternation of the order in which the monomers are coordinated in combination with the *cis*-migration mechanism of insertion in the Ni–R bond ensures the exceptional selectivity of the codimerisation reaction.

Another version of the alternation mechanism has been proposed.[1,77,78] It has been suggested that the order in which the monomers are coordinated is determined by the number of vacancies in the coordination sphere of the metal. In the presence of a single free site, the olefin is more readily coordinated because it is more basic than the diene. In the presence of two vacancies, the coordination of the bidentate diene is more favourable. This mechanism explains satisfactorily the possibility of the formation of alternating copolymers of butadiene with α-olefins, but it can hardly operate in the codimerisation of olefins, each of which is capable of occupying only one coordination site. Apparently, depending on the nature of the metal, its ligand environment, and valence state as well as the geometry of the active complex, both versions of the alternation mechanism are possible.

Finally, one should point out that the mode of codimerisation is affected very strongly by the possibility of additional conjugation of any type. In the case of propene the greater probability of σ, π conjugation in the complex (X) compared with (XI) is apparently the main cause of the addition of nickel to the second carbon atom (contrary to the Markovnikov rule), which leads to the preferential formation of 4-phenylpent-2-ene:



In the presence of bulky ligands, the probability of σ,π conjugation diminishes, as a result of which there is in some cases an increase of the contribution by the addition of nickel to the first carbon atom and hence an increase of the content of the "tail-to-tail" adduct—2-methyl-3-phenylbut-1-ene.[27,29,30] The same effect probably occurs also in the dimerisation of propene, where the bulky phosphorus-containing ligands direct the process towards the formation of 2,3-dimethylbut-1-ene.[4–7]

Systematic studies[5,6] have shown that the influence of phosphines on the mode of addition of propene to the Ni–C and Ni–H bonds is determined to a large extent by steric factors, because among the *ortho*-, *meta*-, and *para*-substituted triphenylphosphines, an increase of the yield of 2,3-dimethylbut-1-ene and a decrease of the yield of hexenes are promoted solely by the *ortho*-substituted compounds. In the presence of aliphatic phosphines with similar electron-donating properties containing large organic groups, nickel forms a bond preferentially with the first carbon atom of propene in the first stage of the addition of propene to Ni–C, while in the absence of ligands it forms a bond preferentially with the second carbon atom [C(2)].

This has been explained by Henrici-Olivé and Olivé.[79] The authors suggest that, in the absence of steric hindrance by the ligand, the polarity of the double bond of propene is reversed in the coordination of the latter, as a result of which a negative charge appears on C(2). However, there are data according to which the addition of propene to the nickel hydride centres proceeds preferentially in the direction of Ni–C(2) even in the presence of phosphorus-containing ligands.[5,6] Consequently, the formation of the Ni–C(2) bond is presumably caused by the energy gain owing to the additional conjugation of the σ,π or $d_\pi p_\pi$ type and not by the reversal of the polarity of the double bond. On the other hand, if such interaction is blocked by the bulky groups of the ligand, then the addition takes place in accordance with the Markovnikov rule, i.e. in the direction Ni–C(1). Overall, the addition takes place via the S_ECi mechanism when both carbon atoms in the coordinated olefin molecule carry a partial positive charge.

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